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# OF THE USSR

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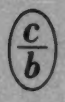

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# BUTYLRHODAMINE–A NEW REAGENT FOR PHOTOMETRIC DETERMINATION, EXTRACTION, PRECIPITATION, AND COPRECIPITATION OF ELEMENTS

V. I. Kuznetsov and L. I. Bol'shakova

The V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry, Academy of Sciences, USSR, Moscow

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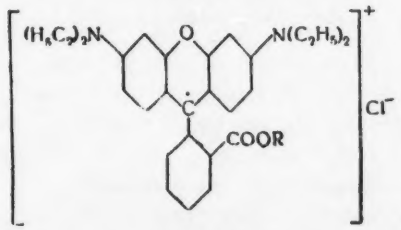
Many elements which can form complex hydrophobic anions such as $Zn(SCN)_4^{2-}$, $SbCl_6^-$, $HgBr_4^{2-}$ and similar anions, give so-called "colored solid phase reactions" [1]. Salts of heavy colored organic cations serve as reagents. As a result of these reactions colored precipitates of sparingly soluble salts appear, which are formed by the cation of the reagent and the complex anion of the element. These sparingly soluble salts can often be extracted by organic solvents [2, 3]; this fact is made use of for the extraction or the extraction-photometric determination of the elements. Finally, in the form of these compounds, the elements can be coprecipitated with organic coprecipitants [4-6]. Thus the reagents adopted are used for the photometric determination, precipitation, coprecipitation, and extraction of the elements.

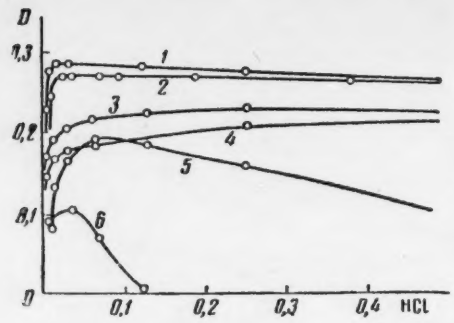
Many reagents have been recommended for this purpose, they include: methyl violet, crystal violet, rhodamine B, p-dimethylaminobenzene, anthrazo and a number of others [7-10]. These reagents are not universal. The action of each is limited more or less to a narrow pH range, and sometimes even the field in which they are applied is limited. When a given reagent is suitable for color solid phase reactions or coprecipitation it is not always suitable for extraction, etc.

The greatest difficulties arise in connection with the small operating pH range. Thus, at acidities greater than 0.1-0.4 N, methyl violet is no longer suitable. In strongly acid solutions p-aminoazobenzene is suitable, but at pH> 4 its salts hydrolyze.

The best reagent which is suitable for a wide pH range is rhodamine B, which was first used by Eegriwe [11] for color reactions; other research workers followed him [8].

The authors of the present article have observed that the range of suitable pH values, and, particularly, completeness of precipitation, coprecipitation, and extraction of the elements can be considerably increased when, instead of rhodamine B itself, its ester is used.

Rhodamine B [1]  is the salt of an organic cation containing




Effect of acidity on the sensitivity of colored solid phase reactions of rhodamine B esters. Concentrations: Tl) 0.8 μg/ml (5 μg/ml for methyl violet); reagent) $2 \cdot 10^{-5}$ M ($5 \cdot 10^{-5}$ M for methyl violet). 20 ml cuvette, green filter. 1) Isoamylrhodamine + $TlCl_4^-$; 2) butylrhodamine + $TlCl_4^-$; 3) benzylrhodamine + + $TlCl_4^-$; 4) octylrhodamine + $TlCl_4^-$; 5) rhodamine 3 B + $TlCl_4^-$; 6) methyl violet + $TlCl_4^-$.

a carboxyl group. The latter to some extent weakens the basic properties of the whole cation, and increases the solubility of the salts formed by rhodamine B, even in acid media. This unfavorable effect of the carboxyl group can be eliminated by esterifying it. When rhodamine B is esterified with not too light an alkyl radical, then it is possible, at the same time, to depress the solubility of the salts formed even further in line with the so-called "weighting" effect. The latter could be achieved by introducing heavy hydrophobic substituents into some other places in the rhodamine B molecule as well, e.g., substituting the $C_2H_5$ on the nitrogen atom by heavier alkyl radicals. Such substitutions, however, weaken the basic properties of the cation, apart from difficulties connected with the synthesis of such reagents. The introduction of heavy substituents into the aromatic nucleus complicates the synthesis to a very marked extent. Thus, alkylation of the carboxyl group would appear to be the only practical way of improving rhodamine B.

The ethyl ester of rhodamine B which is used as a dye under the name rhodamine 3B is a more valuable reagent than rhodamine B. It is natural to expect that other esters of rhodamine B may have equal or even better properties. In order to find out which of the possible esters have the most valuable properties as a reagent, we have synthesized and examined a number of esters of rhodamine B, they include: the n-butyl, isoamyl, n-octyl, and benzyl esters of rhodamine B.

With respect to the operating pH range within which colored solid phase reactions can be carried out, all these esters are superior to rhodamine B and are of equal value among each other. In order to compare the reagents according to this index, a study was made of the effect of the acidity on the sensitivity of colored solid phase reactions.

The anion $TlCl_4^-$ was used as test object, while for all the reagents tested, apart from methyl violet, which was taken as a reference, the conditions used were the same. The thallium concentration was 0.8 μg/ml while the concentration of the reagents was $2 \cdot 10^{-5}$ M. In the case of methyl violet, the thallium concentration was 5 μg/ml, while the methyl violet concentration was $2 \cdot 10^{-5}$ M. Into a 25 ml standard flask was introduced a solution of $Tl_2(SO_4)_3$ in 0.1 N HCl and the requisite amount of hydrochloric acid, 10-15 ml of distilled water was added, and the whole thoroughly mixed; 1.0 ml of the reagent was then added gradually and the solution finally made up to the mark with water. Five minutes after mixing, the light absorption of the solution obtained was measured in a 20 ml cuvette on a FÉK-N-54 photoelectrocolorimeter fitted with a green No. 5 filter (maximum transmission at 536 mμ), relative to a solution of the reagent of the same concentration. The results obtained are shown in the Fig., which also includes results for methyl violet for comparison.

In order to compare the reagents with respect to their suitability for extraction, the partition coefficients were determined during the extraction of thallium from solutions with varying acidities. Thallium was extracted in the form of the salt formed between the anion $TlCl_4^-$ and the cation of the rhodamine B ester, with an equal volume of toluene. The concentrations of thallium and of the reagents were the same as those used in the experiments on the effect of acidity on the sensitivity of the colored solid phase reactions.

Into a test tube with a ground-glass stopper was introduced the requisite amount of hydrochloric acid, and water was added so that the final volume was 2 ml; $Tl(NO_3)_2$ solution labelled with $Tl^{204}$ was added in an amount such that the count rate was about 15,000 cpm, this was followed by the reagent and the whole thoroughly mixed, 2.0 ml of toluene was added and the mixture shaken vigorously for 3 min. After the mixture had separated out into layers, aliquots were taken from the upper and lower layers, and placed in 20 mm tall porcelain crucibles with an upper diameter of 23 mm; they were evaporated on a water bath and the activity determined on a torsion β-counter. The partition coefficients determined, which are ratios of the thallium concentration in the

TABLE 1

Effect of Acidity on the Extraction of Thallium. Concentrations: Tl) 0.8 μg/ml (5 μg/ml for methyl violet). Reagent: $2 \cdot 10^{-5}$ M

| Reagent | HCl concentration, M | Partition coefficient | Reagent | HCl concentration, M | Partition coefficient |
|---|---|---|---|---|---|
| Methyl violet | 0,5 | 0,82 | Benzylrhodamine | 0,5 | 7,1 |
| | 1,0 | 0,10 | | 1,0 | 7,8 |
| | 2,0 | 0,004 | | 2,0 | 16,7 |
| Rhodamine B | 0,5 | 3,7 | Octylrhodamine | 0,5 | 11 |
| | 1,0 | 1,4 | | 1,0 | 13 |
| | 2,0 | 1,2 | | 2,0 | 18 |
| Astrafloxine | 0,5 | 5,8 | Isoamylrhodamine | 0,5 | 7,9 |
| | 1,0 | 4,2 | | 1,0 | 17 |
| | 2,0 | 4,2 | | 2,0 | 28 |
| Rhodamine 3B | 0,5 | 5,4 | Butylrhodamine | 0,5 | 4,2 |
| | 1,0 | 4,3 | | 1,0 | 11 |
| | 2,0 | 3,0 | | 2,0 | 26 |

organic solvent layer to its concentration in the aqueous layer, are given in Table 1. Each value is the mean of 2-3 determinations.

The isoamyl and butyl esters of rhodamine B have been used for the coprecipitation of quadrivalent plutonium [12, 13]. The results of the coprecipitation given in Table 2 are taken from this work.

## DISCUSSION OF RESULTS

A comparison of the results obtained for esters of rhodamine B as reagents, as a function of the dimensions of the alkyl radical, shows that the highest extraction and coprecipitation, and the highest sensitivity of the colored solid phase reactions, are achieved in practice when a $C_4$ alkyl is used.

Bearing in mind the difficulty of synthesizing esters with heavier alkyls, the most valuable representative of this group with respect to the sum total of the indices is the butyl ester which we propose to call "butylrhodamine."

The reagent butylrhodamine can be recommended for colored solid phase reactions, precipitation, coprecipitation, and extraction of elements which are capable of forming complex, not-too-hydrophilic anions.

### Synthesis of Rhodamine B Esters

In developing methods for preparing rhodamine B derivatives, the method used for preparing rhodamine 3B from rhodamine B and ethyl chloride [14] was used as a basis, the only difference being that the alkyl bromide was used instead of the alkyl chloride. The alkyl bromides were obtained by the use of hydrobromic and sulfuric acids [15].

The butyl ester of rhodamine B. Fifty g of commercial rhodamine B hydrochloride is dissolved in 200 ml of water on heating on a boiling water bath. The dark-rose, hot solution is filtered in order to remove accidental contamination, and to the filtered solution is slowly added with stirring a solution of 25 g of NaOH in 100 ml of water. The sodium salt of rhodamine B which is precipitated is filtered off from the hot (!) solution on a Buchner funnel and dried in air.

Thirty g of the completely dry sodium salt of rhodamine B is placed in a round-bottom flask, and 54 ml of n-butyl bromide and 200 ml of butanol added; the mixture is heated under reflux on an oil bath for 10-12 hr, (the temperature of the oil bath is 120°). After cooling, the reaction mass is transferred to a porcelain basin and excess n-butyl bromide and butanol removed by evaporation on a water bath.

a) Butylrhodamine hydrochloride. The product remaining after evaporating off the butyl bromide and butanol is dissolved in hot water, and the still-hot solution acidified with concentrated hydrochloric acid until the solution gives an acid reaction to congo red. The butylrhodamine hydrochloride which separates out in a sirupy form on cooling is removed from the mother liquor by decantation and is dried at 35-40°.

TABLE 2

Coprecipitation of $Pu^{IV}$ by the "Nitrate Mechanism." Volume of the Original Solutions 100 ml. Plutonium Dilution $1:1\cdot10^9$ (0.1 μg Pu in 100 ml). In Each Experiment 200 mg of the Test Coprecipitant was Added in the Form of Its 1% Solution

| Coprecipitant | Concentration | | Coprecipitation |
|---|---|---|---|
| | $NH_4NO_3$, % | $HNO_3$, M | Pu, % |
| Methyl violet chloride | 30 | 0.6 | 4 |
| | 50 | 0.6 | 8 |
| Nitron, acetate | 30 | 0.6 | 8 |
| | 50 | 0.6 | 13 |
| Diphenylguanidine, acetate | 30 | 0.6 | 14 |
| | 50 | 0.6 | 18 |
| Rhodamine B, chloride | 30 | 0.6 | 21 |
| | 50 | 0.6 | 64.66 |
| | 50 | 1.8 | 74.75 |
| Diantipyrylphenylmethane, hydrochloride | 30 | 0.6 | 20 |
| | 50 | 0.6 | 30 |
| | 50 | 1.8 | 43.48 |
| n-Phenylene-bis-(diantipyrylmethane)-hydrochloride | 30 | 0.6 | 40 |
| | 50 | 0.6 | 60 |
| | 50 | 1.8 | 90.92 |
| Amyl ester of rhodamine B, chloride | 30 | 0.6 | 38 |
| | 50 | 0.6 | 80 |
| | 50 | 1.8 | 90.95 |
| Butyl ester of rhodamine B (butylrhodamine, rhodamine 5B) chloride | 30 | 0.6 | 30 |
| | 50 | 0.6 | 92.95 |
| | 50 | 1.8 | 99.100 |
| | | | 101 |

b) Butylrhodamine nitrate. The product remaining after evaporating off the butyl bromide and butanol is dissolved in hot water, the solution is cooled and acidified with concentrated nitric acid until an acid reaction to congo red is given; the solution is then neutralized with ammonia. The sirupy butylrhodamine nitrate which separates out is removed from the mother liquor by decantation and is dried at 35-40°.

The hydrochloride and nitrate salts of butylrhodamine are dark raspberry-red crystals, which are soluble in water, alcohol, and acetone; they are insoluble in benzene and toluene. They are not extracted from aqueous solutions by benzene, toluene, and chloroform.

1.87 g of the hydrochloride and 1.37 g of the nitrate salt dissolve in 100 ml of water at 20°.

Aqueous solutions of the hydrochloride and nitrate salts of butylrhodamine have an intensely rose color; when colored solid phase reactions are carried out, blue colors develop. The color does not change appreciably on acidifying to 0.1 N HCl.

Free chlorine decolorizes the solution, free bromine changes the color to a turbid orange; $H_2O_2$, $SnCl_2$, and $TiCl_3$ have no effect.

## SUMMARY

Butylrhodamine (the butyl ester of rhodamine B) is recommended as a reagent for carrying out colored solid phase reactions and precipitation, for coprecipitation and extraction of elements which are capable of forming hydrophobic complex anions in acid media. Butylrhodamine is suitable for work in a wider acidity range than, for example, methyl violet or rhodamine B.

The sparingly soluble blue salts which are formed between butylrhodamine and the complex anions of elements can be extracted with $C_6H_6$, $CHCl_3$, etc; the extracts are rose colored.

The synthesis of butylrhodamine is described; it is prepared by the action of butyl bromide on the anhydrous sodium salt of rhodamine B.

## LITERATURE CITED


[1] V. I. Kuznetsov, Uspekhi Khim. 18, 75 (1949).

[2] V. I. Kuznetsov, Uspekhi Khim. 23, 672 (1954).

[3] G. H. Morrison and H. Freiser, Anal. Chem. 30, 632 (1958).

[4] V. I. Kuznetsov, Zhur. Anal. Khim. 9, 199 (1954).*

[5] V. I. Kuznetsov and G. V. Myasoedova, Zhur. Anal. Khim. 10, 211 (1955).*

[6] V. I. Kuznetsov and T. G. Akimova, Zhur. Anal. Khim. 13, 79 (1958).*

[7] V. I. Kuznetsov, Zhur. Anal. Khim. 1, 259 (1946).

[8] V. I. Kuznetsov, Doklady Akad. Nauk SSSR 52, 231 (1946).

[9] V. I. Kuznetsov, Doklady Akad. Nauk SSSR 41, 113 (1946).

[10] M. A. Popov, Zavodskaya Lab. 13, 618 (1947).

[11] E. Eegriwe, Z. anal. Chem. 70, 400 (1927).

[12] V. I. Kuznetsov and T. G. Akimova, Radiokhimiya 2, 357 (1960).

[13] V. I. Kuznetsov and T. G. Akimova, Atomnaya Energiya 8, 148 (1960).*

[14] German Patent 66238; Frdl. 3, 177.

[15] Collection: Synthesis of Organic Preparations, edited by Academician Kazanskii (IL, Moscow, 1949, Vol. I) p. 108.


* Original Russian pagination. See C. B. Translation.

# A STUDY OF THE SOLUBILITY OF ZIRCONIUM, THORIUM, AND URANIUM PHENYLARSONATES

V. A. Mikhailov

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Original article submitted November 30, 1959

Precipitation of zirconium by means of phenylarsonic acid is carried out from strongly acid solutions [1, 2] while thorium is precipitated from acetic acid solutions [1, 3]. As far as we know, no quantitative studies have been made of the solubility of zirconium and thorium phenylarsonates. Usually, zirconium is precipitated in the form of a basic phenylarsonate [2]. The reaction leading to the formation of uranium phenylarsonates and the properties of the latter have not been studied in practice. There are indications that under the conditions used for the precipitation of zirconium and other quadrivalent metals, sexivalent uranium is not precipitated [3-5]. The pH at the beginning of the precipitation of uranyl by phenylarsonic acid has been established as 1.5, however, no indications were given of the concentrations used [6]. It is recommended that uranium be precipitated at pH 1-3 [3].

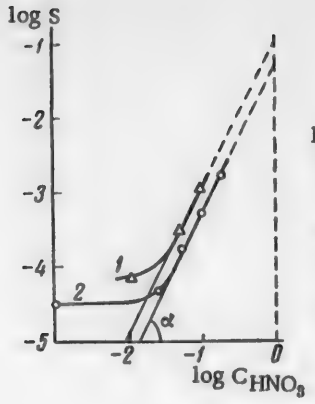
Reagents and experimental technique. Nitric acid solutions of zirconium nitrate marked with $Zr^{95}$, and of thorium nitrate marked with $Th^{229}$ were used in the work. The solution of zirconium nitrate was heated beforehand in concentrated nitric acid for 30 min at 100° in order to convert zirconium into the nonhydrolyzed form. The preparation of $Zr^{95}$ was used not more than 5 hours after its purification from the daughter element $Nb^{95}$. The nitric acid solutions of uranyl nitrate marked with $U^{233}$ had a specific activity of 5000 disintegrations/min/mg. The latter was used in the course of not more than 30 days after extraction purification from the daughter radioactive elements. Quadrivalent uranium was obtained in acid solution by addition of five times its amount of rongalite [7].

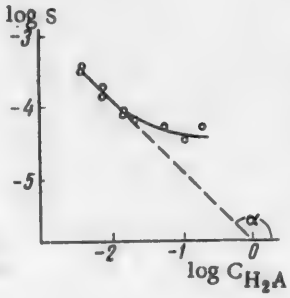
The phenylarsonic acid preparation, "pure" grade, contained not less than 95% of the main component. The absence of arsenite in the preparation was established by a qualitative reaction in a carbonate medium with starch and iodine.

The solubility of the metal phenylarsonates was determined mainly by a precipitation technique, when the equilibrium solubilities are reached from saturated solutions in the presence of a precipitate [8, 9]. After mixing all the requisite reagents, the solutions were heated at 70-90° for about 15 min in order to make the precipitate coarser; the solutions together with the flock-like precipitates which separated out were then cooled for about an hour at 18 ± 3°. In certain, special cases, the solubility was also determined by the method of dissolving the precipitates obtained earlier. The precipitates were mixed in the solutions for 4-6 hours. In these cases the precipitates used were those that had been precipitated and made coarser by heating, i.e., precipitates having approximately the same structure as the precipitate used in the first technique.

The precipitates were removed by centrifugation, and the concentrations of zirconium, thorium, and uranium were determined radiometrically in the centrifugate. The uranium concentration was also determined by a luminescence method.

Solubility of uranium phenylarsonates. The phenylarsonates of quadrivalent and sexivalent uranium are pale-green in color.



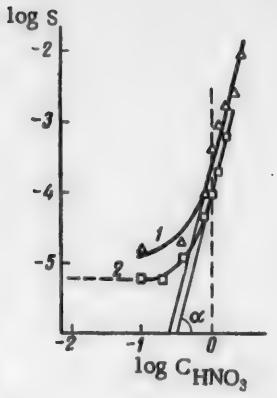




Fig. 1. Fig. 2. Fig. 3.

Fig. 1. Effect of acidity on the solubility of uranium (VI) phenylarsonate at a phenylarsonic acid concentration of 0.08 M. 1) Ammonium nitrate was not added; 2) ammonium nitrate 2 M.

Fig. 2. Effect of phenylarsonic acid concentration on the solubility of uranium (VI) phenylarsonate at a nitric acid concentration of 0.02 M.

Fig. 3. Effect of acidity on the solubility of uranium (IV) phenylarsonate at a phenylarsonic acid concentration of 0.04 M. 1) Ammonium nitrate was added until a concentration of 2 M with respect to the $NO_3^-$ ion was reached; 2) ammonium nitrate was not added.

In the experiments on the determination of the solubility of the phenylarsonate of sexivalent uranium, the original concentration of the uranium was $2 \cdot 10^{-3}$ M. The effect of the acidity of the medium and the phenylarsonic acid concentration on the solubility is shown within logarithmic coordinates in Figs. 1 and 2. The effect of these factors on the solubility of the phenylarsonate of quadrivalent uranium is shown in Figs. 3 and 4. In the latter experiments the original uranium concentration was $10^{-3}$ M; only in experiments in which the nitric acid concentration was higher than 1 M was the uranium concentration $10^{-2}$ M.

On the solubility curves there is a point where there is a fairly sharp change from the inclined straight-line sections, coinciding with the tangents, to almost horizontal sections of the curves. The lowest values of the solubilities observed in the given experiments were those for the phenylarsonate of sexivalent uranium which was $3 \cdot 10^{-5}$ M and for the phenylarsonate of quadrivalent uranium which was about $1 \cdot 10^{-5}$ M. It is obvious that these values of the solubilities of the compounds will determine the loss of uranium in filtrates, in the case of analytical and other applications of reactions involving the precipitation of these compounds. Presumably, these values are those of the solubility of the nondissociated molecular forms of the compounds in water.

The curves obtained enable one to establish the following conditions for the most complete precipitation of uranium in the form of its phenylarsonates: for sexivalent uranium, at a phenylarsonic concentration of 0.08 M, the acidity of the solution should not exceed 0.01 M, while for quadrivalent uranium at a reagent concentration of not less than 0.04 M, the acidity should be higher than 0.3 M.

On the inclined sections of the solubility curves, it is obvious that in the case of sexivalent uranium the solubility depends on the second power of the hydrogen ion concentration of the solution (the tangent of the angle made by the straight line in Fig. 1 with the horizontal is approximately 2), and on the first power of the phenylarsonic acid concentration (tangent $\alpha$ in Fig. 2 is approximately 1). While in the case of quadrivalent uranium the solubility depends on the fourth power of the hydrogen ion concentration (Fig. 3) and on the second power of the phenylarsonic acid concentration (Fig. 4).

It follows from this that precipitation of uranium ions proceeds according to the following schemes:

$$UO_2^{2+} + H_2A \rightleftarrows \downarrow UO_2A + 2H^+; \qquad U^{4+} + 2H_2A \rightleftarrows \downarrow UA_2 + 4H^+;$$

where $H_2A$ is phenylarsonic acid.

The solubility of zirconium and thorium phenylarsonates. The effect of the acidity of the solution on the solubility of zirconium and thorium phenylarsonates for a constant concentration of the reagent is shown in Fig. 5. In Table 1 are shown some additional results on the solubility of zirconium phenylarsonate in water, in hydrochloric and sulfuric acid solutions, and on the effect of phenylarsonic acid on the solubility of thorium phenylarsonate. In addition, Table 1 also contains results obtained by the method of dissolving the precipitates formed beforehand. In experiments on precipitation, the original concentration of the zirconium or thorium was $10^{-3}$ M, apart from the last point on curve 1, Fig. 5 and experiment 7, Table 1, where the original concentration was $10^{-2}$ M.

Determination of the composition of zirconium phenylarsonate formed in 1 M nitric acid solutions under the conditions used in our work showed that: the precipitate, washed with water and dried at 200°, weighed 150.0 mg; on subsequent calcination at 1100°, 36.0 mg of zirconium dioxide was obtained, which corresponds to 27.0 mg or 18% of zirconium. The calculated zirconium content for the normal phenylarsonate is 18.7%.

Thorium phenylarsonate precipitated at pH 1 and dried at 200°, weighed 41.0 mg; on calcining at 1100°, 16.5 mg of thorium dioxide was obtained; this corresponds to 14.5 mg or 36.5% thorium. The calculated value for thorium in the normal phenylarsonate is 36.8%.

TABLE 1

| Expt. No. | Compound | Acidity of the solution | Phenylarsonic acid, M | Solubility, $M \cdot 10^5$ | $K_T$ |
|---|---|---|---|---|---|
| 1 | Zirconium phenylarsonate | Water | — | 0,2* | — |
| 2 | Ditto | 0,2 *M* $HNO_3$ | 0,02 | 0,5* | — |
| 3 | » » | 2,2 *M* HCl | 0,01 | 0,8 | — |
| 4 | » » | 3,3 *M* HCl | 0,01 | 0,8 | — |
| 5 | » » | 4,4 *M* HCl | 0,01 | 0,8 | — |
| 6 | » » | 6,7 *M* HCl | 0,008 | 14 | 11,3 |
| 7 | » » | 10 *M* HCl | 0,003 | 900 | 11,1 |
| 8 | » » | 1 *M* $H_2SO_4$ | 0,022 | 0,2 | — |
| 9 | » » | 2 *M* $H_2SO_4$ | 0,022 | 1,7 | — |
| 10 | » » | 3,4 *M* $H_2SO_4$ | 0,022 | 37 | ~9 |
| 11 | Thorium phenylarsonate | 0,005 *M* $HNO_3$ | 0,02 | 1,1* | — |
| 12 | Ditto | 0,3 *M* $HNO_3$ | 0,05 | 95 | 3,5 |
| 13 | » » | 0,3 *M* $HNO_3$ | 0,03 | 146 | 3,8 |
| 14 | » » | 0,3 *M* $HNO_3$ | 0,02 | 172 | 4,1 |

* The solubility was determined by the method of dissolving the precipitate obtained beforehand.

It is clear from the solubility curves in Fig. 5, as in the case of uranium phenylarsonates, that there is a sharp change from the inclined, almost linear sections, to the horizontal sections of the curves. It was shown that the lowest solubility of zirconium phenylarsonate in acid solutions, as determined by different methods — precipitation and dissolution — almost coincides with its solubility in water (compare experiments 1-5 and 8 in Table 1 and curve 2, Fig. 5).

The solubility curves shown, and the results given in Table 1, allow one to establish conditions for ensuring most complete precipitation when phenylarsonic acid is used as precipitant: for zirconium at a reagent concentration of 0.005 M, the acidity of the solution should not be less than 2 M, while for thorium at a reagent concentration of 0.08 M, the acidity of the solution should not be higher than 0.03 M. In the case of zirconium, the acidity can be increased to 4 M and higher as long as the phenylarsonic acid concentration exceeds 0.01 M. While if zirconium is precipitated in a sulfuric acid medium, then the acidity of the solution should not exceed 2 M even when the reagent concentration is 0.02 M.

As is evident from Fig. 5, the tangent of the angle made by the tangents to the solubility curves of zirconium and thorium phenylarsonsates (tangent $\alpha$) is equal to 4, i.e., their solubility depends on the fourth power of the hydrogen ion concentration. The results given above on the determination of the composition of the

compounds confirms that formation of the normal phenylarsonates occurs. Accordingly, precipitation of $Zr^{IV}$ and $Th^{4+}$ proceeds according to the scheme:

$$M^{IV} + 2H_2A \rightleftarrows MA_2 + 4H^+;$$

where $H_2A$ is phenylarsonic acid.

Calculation of the reaction constants. Since the tangents to the solubility curves can be interpreted by means of the schemes given above for the reactions, they can be used for calculating the constants of the precipitation reaction, because the formation constant of the insoluble phenylarsonates can be expressed as follows:

$$K_r = \frac{[H^+]^n}{[M^{n+}][H_2A]^{\frac{n}{2}}},$$

where $K_r$ is the constant of the formation reaction, n is the charge on the cation; by taking logarithms and transforming this expression we obtain:

$$[M^{n+}] = \log S = \lg \frac{1}{K_r [H_2A]^{\frac{n}{2}}} + n \log [H^+],$$

for $[H_2A]$-const. (tangents to curves in Figs. 1, 3, and 5), and

$$\log [M^{n+}] = \log S = \log \frac{[H^+]^n}{K_r} - \frac{n}{2} \log [H_2A]$$

for $[H^+]$ approximately equal to $[HNO_3]$-const (tangents to the curves in Figs. 2 and 4). Here S is the analytically determined concentrations of the metals, which, as follows from Figs. 1-5, can be equated to the concentrations of $M^{n+}$ cations, if the value of the solubility is equal to not less than $10^{-4} - 5 \cdot 10^{-5}$ M.

Taking into account the fact that the equations given above for the straight lines are the equations of the corresponding tangents, it is possible to determine their free terms from the value of the segment of the ordinate for zero values of the abscissa, and then calculate $K_r$.

Since it is difficult to calculate activity coefficients at high salt concentrations, the concentration constants of the reaction are given here. The corresponding ionic strength of the solutions was calculated by the normal method from the concentrations of the strong electrolytes present in solution: ammonium nitrate, nitric or hydrochloric acid. In a series of experiments in which the acidity was varied, an evaluation was made of the mean value of the ionic strength for points corresponding to the linearly sloping sections of the curve, i.e., for sections coinciding with the tangents; in these cases the ionic strength is indicated approximately.

Thus, the following values were found for uranium (VI) phenylarsonate: according to Fig. 1, log $K_r$ = 2.0 (ionic strength $\mu$ approximately 0.1) and log $K_r$ = 2.4 ($\mu$ = 2), and according to Fig. 2, log $K_r$ = 2.4 ($\mu$ = 0.02), mean log $K_r$ = 2.2 ± 0.2; while for uranium (IV) phenylarsonate, according to Fig. 3, log $K_r$ = 6.8 ($\mu$ approximately 1) and log $K_r$ = 6.5 ($\mu$ = 2), and according to Fig. 4, log $K_r$ = 6.1 ($\mu$ = 0.5), mean log $K_r$ = 6.5 ± 0.3. Since a linear relationship is not observed between log $K_r$ and the ionic strength ($\mu$), according to the results given above, the mean value of $K_r$ is calculated. According to Fig. 5, for zirconium phenylarsonate log $K_r$ = = 11.8 ($\mu$ approximately 5, nitric acid media), while for thorium phenylarsonate log $K_r$ = 3.7 ($\mu$ approximately 0.5).

According to the results of a series of experiments (Table 1) it is also possible to calculate log $K_r$ for zirconium and thorium phenylarsonates. In this case use can only be made of those points for which, as noted above, the solubility exceeds $10^{-4}$ M, i.e., when the analytically determined concentration of the metal can be equated to the concentration of the cation. The average value of log $K_r$ calculated in this way for zirconium phenylarsonate in hydrochloric acid solutions is log $K_r$ = 11.2 ± 0.1. Since the difference for nitric and hydrochloric acid solutions is not great, it is possible to take the mean value log $K_r$ = 11.5 ± 0.3 ($\mu$ from 4 to 10).

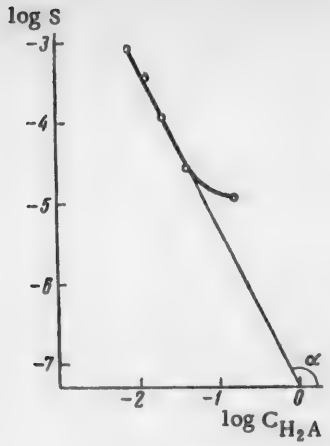



Fig. 4.

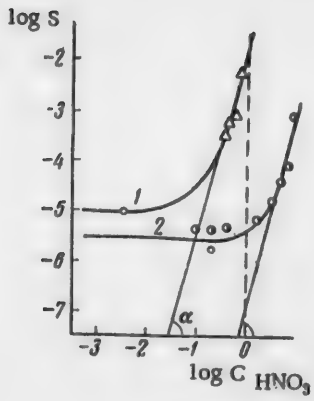



Fig. 5.

Fig. 4. Effect of phenylarsonic acid concentration on the solubility of uranium (IV) phenylarsonate at a nitric acid concentration of 0.5 M.

Fig. 5. Effect of the acidity of the solutions on the solubility of zirconium and thorium phenylarsonates. 1) Solubility curve of thorium phenylarsonate at a phenylarsonic acid concentration of 0.08 M; 2) solubility of zirconium phenylarsonate at a phenylarsonic acid concentration of 0.005 M.

TABLE 2

| Compound | Lowest solubility, M | log $K_r$ | $pL_s$ | $pK_{Inst.}$ |
|---|---|---|---|---|
| Uranium (VI) phenylarsonate | $3 \cdot 10^{-5}$ | 2,2±0,2 | 14 | 9,5 |
| Uranium (IV) phenylarsonate | $1 \cdot 10^{-5}$ | 6,5±0,3 | 30,5 | 25,5 |
| Zirconium phenylarsonate | $(0,5 \pm 0,2) \cdot 10^{-5}$ | 11,5±0,3 | 35,5 | 30 |
| Thorium phenylarsonate | $1 \cdot 10^{-5}$ | 3,8±0,3 | 28 | 23 |

On the other hand, the formal constant of the reaction in sulfuric acid media, which can be calculated on the basis of the results of experiment 10, Table 1, differs very strongly: log $K_r$ is about 9.

On the basis of the results of experiments 12-14, Table 1, it is possible to calculate $K_r$ for the formation of thorium phenylarsonate, log $K_r = 3.8 \pm 0.3$ ($\mu = 0.3$). The agreement in $K_r$ in both cases is good; mean log $K_r = 3.8 \pm 0.3$.

Following the generally accepted characteristic of sparingly soluble compounds, it is possible to calculate the solubility product $L_s$ of phenylarsonates. Knowing the constant of the acid dissociation of phenylarsonic acid, which is given by $K_{diss} = 10^{-12}$ [10], we have:

$$L_s = [M^{n+}][A^{3-}]^{\frac{n}{3}} = K_{diss}^{\frac{n}{3}}/K_r \quad \text{or} \quad pL_s = \frac{n}{3} pK_{diss} + \log K_r.$$

Further, having assumed that the solubility of phenylarsonates under conditions where the most complete precipitation is observed is determined by the solubility of their undissociated forms $MA_{n/3}$, it is possible to calculate the instability constants of these compounds:

$$K_H = \frac{[M^{n+}][A^{s-}]^{\frac{n}{s}}}{[MA_{\frac{n}{s}}]} = \frac{L_s}{[MA_{\frac{n}{s}}]} \quad \text{or} \quad pK_H = pL_s + \log[MA_{\frac{n}{s}}].$$

The quantitative characteristics of the solubility of uranium, zirconium, and thorium phenylarsonates determined in the course of this work are collected in Table 2.

## SUMMARY

Using the method of labelled atoms, a study has been made of the solubility of the phenylarsonates of sexi- and quadrivalent uranium, zirconium, and thorium in solutions of varying acidity in the presence of phenylarsonic acid. Conditions have been established for ensuring their most complete precipitation, and their solubility has been determined under these conditions: for uranium (VI) phenylarsonate this was found to be $3 \cdot 10^{-5}$M, while for uranium (IV) phenylarsonate it was $1 \cdot 10^{-5}$ M, and for zirconium phenylarsonate $0.5 \pm 0.2 \cdot 10^{-5}$ M and for thorium phenylarsonate $10^{-5}$ M.

The logarithms of the concentration constants of the reactions leading to the formation of the phenylarsonates have been calculated; they were found to be 2.2 ± 0.2 for uranium (VI) phenylarsonate, 6.5 ± 0.3 for uranium (IV) phenylarsonate, 11.5 ± 0.3 for zirconium phenylarsonate, and 3.8 ± 0.3 for thorium phenylarsonate.

## LITERATURE CITED

[1] Rice, Fogg and James, J. Am. Chem. Soc. 48, 895 (1926).

[2] I. P. Alimarin and O. A. Medvedeva, Zavodskaya Lab. 11, 254 (1945).

[3] Collection: Analytical Chemistry of Uranium and Thorium (IL, Moscow 1956) p. 233.

[4] I. P. Alimarin and V. I. Frid, Mikrochemie 23, 17 (1937).

[5] W. F. Hillebrand, G. F. F. Lundell, et al., Practical Textbook on Inorganic Analysis [Russian translation] (Goskhimizdat, Moscow, 1957) p. 583.

[6] G. Pietsch, Mikrochimica acta 161 (1957).

[7] A. A. Grinberg, L. E. Nikol'skaya, G. I. Petrzhak, B. V. Ptitsyn, and F. M. Filinov, Zhur. Anal. Khim. 12, 92 (1957).*

[8] I. V. Pyatnitskii, Zhur. Anal. Khim. 1, 57 (1946).

[9] E. S. Tinovskaya, Zhur. Anal. Khim. 5, 345 (1950).*

[10] D. Pressman and D. H. Brown, J. Am. Chem. Soc. 65, 540 (1943).

* Original Russian pagination. See C. B. Translation.

# THE REDUCING PROPERTIES OF MERCURY

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During studies of electrochemical processes which occur on mercury or amalgam electrodes, due attention is not usually given to the side reactions which accompany the main electrode process. In particular, little attention is given to the direct interaction of mercury with materials reduced on the cathode, and to its anodic oxidation together with the other metals present in the amalgam. Underestimation of side reactions may sometimes lead to a one-sided interpretation of the mechanism of the electrode processes. This interpretation has, in our opinion, been made in attempts to explain the steplike waves in works published on polarography by Shvaer and Sukhi on reduction of selenite and tellurite [1], by Issa on reduction of permanganate [2], and by others on reduction of multivalent ions [3, 4]. Formation of steplike waves is also observed during the reduction of ions having only one degree of oxidation. Their appearance in this case is explained by reduction [5, 6] of complexes with different instability complexes. However, the possibility is not excluded that formation of a complex wave is determined by the superposition of the anodic process of the oxidation of mercury on the cathodic process of the reduction of the ions. The appearance of sparingly soluble materials as the result of side reactions may complicate the polarograms even more [7].

During reduction of metals by amalgams, participation of mercury in the reduction reaction is usually not taken into account either.

The reducing property of mercury is determined by the chemical nature of the anions present in solution and adsorbed on its surface. This was pointed out as long ago as 60 years by Paschen [8].

The effect of anions on the potential of mercury can be seen from Table 1.

A comparison of these results with the values of the solubility products of the corresponding mercury salts, and also with the instability constants of the mercury complexes, graphically shows the connection between the depolarization potential of mercury by one ion or another and the solubility (or stability) of the compounds formed between mercury and the corresponding ion. The lower the solubility the greater the negative potential. The existence of such a relationship permits one to carry out quantitative polarographic determination of certain anions [9, 10].

The kinetics and the mechanism of the anodic oxidation of mercury has been studied to a comparatively small extent. Wakkad [11] has given an equation which expresses the relation between the rate at which mercury dissolves and the extent to which the electrode is polarized. All other values being constant, the equation given by Wakkad takes the form

$$V = \text{const} + \frac{RT}{\alpha ZF} \ln I,$$

where V is the difference between the electrode potential and the equilibrium potential; I is the current density; Z is the number of electrons; and F is the Faraday number.

TABLE 1

Normal Oxidation Potentials of Mercury (Normal Hydrogen Electrode) in Various Media

| Electrode reaction | $E_0$, volt | Electrode reaction | $E_0$, volt |
|---|---|---|---|
| $Hg + H_2O - 2e \rightarrow HgO + 2H^+$ | +0,926 | $2Hg + 2CNS^- - 2e \rightarrow Hg_2(SCN)_2$ | +0,22 |
| $2Hg + SO_4^{2-} - 2e \rightarrow Hg_2SO_4$ | +0,615 | $2Hg + 2Br^- - 2e \rightarrow Hg_2Br_2$ | +0,139 |
| $2Hg + CrO_4^{2-} - 2e \rightarrow Hg_2CrO_4$ | +0,41 | $2Hg + H_2O - 2e \rightarrow Hg_2O + 2H^+$ | +0,123 |
| $Hg + 2IO_3^- - 2e \rightarrow Hg + (IO_3)_2$ | +0,40 | $2Hg + 2I^- - 2e \rightarrow Hg_2I_2$ | −0,041 |
| $2Hg + CO_3^{2-} - 2e \rightarrow Hg_2CO_3$ | +0,32 | $Hg + 4CN^- - 2e \rightarrow Hg(CN)_4^{2-}$ | −0,37 |
| $2Hg + 2Cl^- - 2e \rightarrow Hg_2Cl_2$ | +0,268 | $Hg + S^{2-} - 2e \rightarrow HgS$ | −0,70 |

Thus, the relationship between the logarithm of the current strength and the potential, during anodic dissolution of mercury, is expressed by a straight line. However, according to this author, this relation is only preserved at very low current densities.

Cousens, Ives, and Pittman [12-14] have studied the mechanism of the anodic oxidation of mercury. They subjected a mercury electrode to polarization by an interrupted direct current of low value. In the breaks between the individual current impulses, micropolarization tests were carried out (forward and reverse) in order to determine the extent of the reversibility of the electrode. They found that a mercury electrode in a hydrochloric acid solution behaves itself irreversibly, even after passing a fairly large amount of electricity through it, when a precipitate of $Hg_2Cl_2$ is formed. The irreversibility was confirmed by the existence of a hysteresis loop between the ascending and descending branches of the polarization curve. But, after a long interval between such impulses, the electrode became reversible again. It was established that the changes which occur in the potential of the mercury electrode with changes in the amount of electricity passed through the solution are not linear; this follows from the fact that the curve passes through a maximum. The potential of the maximum is several millivolts more positive than the potential of the reversible calomel electrode. It was also found that in order to reach the potential of the calomel electrode, it is necessary to expend a considerably greater amount of electricity than the theoretical amount. Their research led the authors to the conclusion that the primary electrode reaction during anodic polarization of mercury in hydrochloric acid solutions (current density 0.25 $\mu a/cm^2$) is the formation of mercuric ions. Calomel is then formed as the result of a secondary reaction: $Hg^{2+} + Hg^0 \rightarrow Hg_2^{2+}$. At very low current densities generation of $Hg_2^{2+}$ and $Hg^{2+}$ in equilibrium concentration should also occur, since the electrode in this case deviates only insignificantly from the equilibrium state. Application of higher current densities does not alter the mechanism of the process. However, the rapid covering of the mercury surface by $Hg_2Cl_2$ leads to passivation of the electrode and to a discharge of chlorine ions. Subsequently, the liberated chlorine oxidizes the $Hg_2Cl_2$ and depassivizes the electrode.

The presence in solution of ions or molecules which are capable of being reduced on the dropping-mercury electrode may complicate or modify the over-all electrode process. It is known that the reduction potentials of many anions on the dropping-mercury electrode are shifted towards more negative values as compared with their potentials on solid electrodes, particularly platinum ones. This may be explained on the grounds that at those potentials at which anions are reduced on a platinum electrode, anodic oxidation of mercury occurs at the same time on a mercury electrode. As a result of the superposition of the latter process on the reduction of the anions, the cathodic wave may disappear completely, when the oxidation current of mercury exceeds the cathodic current for the reduction of the anions. In actual fact, in this case direct interaction of mercury with the reduced anions will occur. In all cases when the rate at which mercury is oxidized anodically is higher than the rate at which the anions are reduced, the cathodic wave for the reduction of the anions will be absent, and will only appear at those potentials at which the anodic oxidation of mercury ceases. The wave obtained at these potentials will correspond either to the direct reduction of the given ion, or the reduction of mercury ions formed as a result of the interaction of metallic mercury with reducing ions. Opinion on this point differs. Thus, Simpson and Evans [15] assume that in the anodic region metallic mercury in reducing ions of the noble metals gives an equivalent amount of mercury ions, e.g.:

$$2Au^{3+} + 6Hg \rightarrow 2Au^0 + 3Hg_2^{2+}$$

TABLE 2

Interaction of Mercury with Ions in Neutral and Alkaline Solutions*

| Composition of the supporting electrolyte | $MnO_4^-$ | | $CrO_4^{2-}$ | | $S_2O_8^{2-}$ | | $MoO_4^{2-}$ | | $Fe^{3+}$ | | $Cu^{2+}$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | reaction product | potential, volt | reaction product | potential, volt | reaction product | potential, volt | reaction product | potential volt | reaction product | potential, volt | reaction product | potential, volt |
| $NH_4Cl$ | $MnO_2$ $Hg_2Cl_2$ | +0,64 | The mercury forms a sludge | +0,33 | $SO_4^{2-}$ $Hg_2Cl_2$ | +0,65 | 0 | +0,34 | $Fe^{2+}$ $Hg_2Cl_2$ | +0,35 | 0 | +0,37 |
| $NH_4Cl$ $NH_4OH$ | O | +0,41 | The mercury forms a sludge | +0,30 | $SO_4^{2-}$ $Hg_2O$ | +0,31 | 0 | +0,35 | — | — | 0 | +0,33 |
| $(NH_4)_2SO_4$ | $MnO_2$ $Hg_2SO_4$ | +0,66 | The mercury forms a sludge | +0,51 | $Hg_2SO_4$ | +0,68 | 0 | +0,40 | 0 | +0,40 | 0 | +0,51 |
| KSCN | — | — | 0 | +0,21 | — | — | The solution becomes blue-green | +0,13 | $Hg(SCN)_2$ Decolorized no precipitate | +0,30 | — | — |
| KI | — | — | 0 | —0,06 | — | — | The solution becomes blue | —0,09 | $Hg(I)_4^{2-}$ No precipitate | —0,03 | — | — |
| NaOH | $MnO_4^{2-}$ $Hg_2O$ | +0,45 | 0 | +0,15 | $SO_4^{2-}$ $Hg_2O$ | +0,33 | — | +0,12 | — | — | — | — |

* Supporting electrolyte concentration 0.5 M, concentration of the various ions 0.05 M. (1) signifies that the reaction was not studied because of the interaction of the ions with the supporting electrolyte; (0) signifies absence of interaction between the ions and mercury.

TABLE 3

Interaction of Mercury with Certain Ions in Acid Solution

| Ion | HCl 1–6N | | $H_2SO_4$ 1–6 N | |
|---|---|---|---|---|
| | reaction products | reduction potential, volt | reaction products | reduction potential, volt |
| $MnO_4^-$ | $Mn^{2+}$, $Hg_2Cl_2$ $MnO_2$ | +0,22 | $Mn^{2+}$ $Hg_2SO_4$, $MnO_2$ | +0,70 |
| $CrO_4^{2-}$ | $Cr^{3+}$, $Hg_2Cl_2$ | +0,20 | $Cr^{3+}$, $Hg_2SO_4$ | +0,57 |
| $MoO_4^{2-}$ | $Mo^{V}$, $Mo^{III}$, $Hg_2Cl_2$ | +0,16 | Does not react | +0,37 |
| $VO_3^-$ | $V^{4+}$, $Hg_2Cl_2$ | +0,30 | » » | +0,42 |
| $SeO_3^{2-}$ | HgSe, sludge | +0,11 | » » | +0,19 |
| $TeO_3^{2-}$ | HgTe* | +0,17 | » » | +0,18 |
| $Fe^{3+}$ | $Fe^{2+}$, $Hg_2Cl_2$, sludge | +0,19 | » » | +0,68 |
| $Cu^{2+}$ | $Cu_2Cl_2$, $Hg_2Cl_2$, sludge | +0,19 | » » | +0,36 |
| $IO_3^-$ | $Hg_2Cl_2$, CII | +0,21 | » » | +0,31 |
| $S_2O_8^{2-}$ | $Hg_2Cl_2$, $SO_4^{2-}$ | +0,27 | $Hg_2SO_4$ | +0,70 |

* The reduction proceeds in concentrated hydrochloric acid solutions ( > 4N).

while the cathodic wave corresponds to the reduction of mercury ions:

$$Hg_2^{2+} + 2e \longrightarrow 2Hg$$

Kivalo, Laitinen [16] and other authors [17] are of the same opinion. But in a number of cases [2-4, 18, 19] the cathodic waves are explained by the direct reduction of ions ($S_2O_8^{2-}$, $MoO_4^{2-}$, $MnO_4^-$, etc.) on the dropping-mercury electrode. A correct interpretation of the mechanism of electrode processes requires that the whole complex of reactions accompanying polarography should be taken into account. In a particular case, e.g., reduction of tellurium, it is necessary to take into account the depolarization of mercury by tellurite and telluride ions and the formation of precipitates between mercury and these ions.

Thus, a study of the interaction of mercury with a number of ions in the presence of various depolarizers is of undoubted interest. A solution of this question would enable one to give a more correct interpretation of the nature of the polarographic waves and to evaluate the extent to which mercury participates in the reduction of metal ions.

In the work described here, we studied the reduction of copper (II), iron (III), selenite, tellurite, permanganate, dichromate, molybdate, iodate, vanadate, persulfate, and arsenate ions by metallic mercury in various media.

Indications are given in the literature [20-25] on the interaction of mercury with a number of ions. Some of these reactions have been used during the titrimetric determination of oxygen-containing anions for their reduction. However, the reactions indicated have for the most part been carried out in hydrochloric acid solutions. In addition, reduction was effected without any measurements of the potential of mercury. Measurement of this potential during the reduction process is very important, since it permits one to explain the change in the reducing properties of mercury with changes in the experimental conditions.

The supporting electrolytes which we used were neutral, alkaline, and acid materials which shift the oxidation potential of mercury; they included: sulfuric and hydrochloric acids, the ammonium salts of these acids, an ammonia–ammonium chloride mixture, potassium thiocyanate, potassium iodide, and sodium hydroxide.

The reactions were studied by shaking a solution containing the test ions and the appropriate supporting electrolyte with mercury. Shaking was carried out either in a separating funnel or in a special 50 ml vessel

TABLE 4

Cementation of Tellurium by a Cadmium Amalgam

| HCl concentration M | Cd isolated in the solution, g | Te found in the precipitate, g | Yield of Te with respect to Cd, % |
|---|---|---|---|
| 1 | 0,3850 | 0,3366 | 144,7 |
| 2 | 0,3853 | 0,3312 | 142,3 |
| 3 | 0,3805 | 0,3312 | 144,7 |
| 4 | 0,3870 | 0,3360 | 144,7 |
| 5 | 0,3800 | 0,3368 | 142,3 |

Note: Amount of tellurium taken for cementation 0,3310 g; amount of cadmium taken for cementation 0,410 g.

provided with a mechanical stirrer and an attachment for measuring the potential of the mercury. After a 15-20 min shaking the mercury was removed from the solution, any precipitates which might have been formed being filtered off, and the precipitate and solution analyzed separately for their content of reaction products. The precipitates were also analyzed spectrographically. The experimental results are given in Tables 2 and 3.

As is evident from the results given in Table 2, in nonacidified solutions mercury can reduce permanganate, persulfate, and iron(III) ions, and, apparently, molybdate,* while reduction of iron ions only occurs in the presence of strong depolarizers (halide and thiocyanate ions). Iodide ions, as is known, are themselves capable of reducing iron, elemental iodine being formed. On shaking a mixture of iodide and iron (III) solutions with mercury, the iodine is decolorized and reduction of iron proceeds to completion.

In contrast to other ions, permanganate ions are reduced by mercury even in strongly alkaline solutions. Ions such as selenite, tellurite, vanadate, iodate, copper (II), and arsenate do not interaction with mercury in any of the solutions indicated in Table 2. The behavior of mercury in each concrete case is in good agreement with the values of its potentials.

In acid solutions (Table 3) a number of additional ions are included in the reduction reaction: selenite, tellurite, chromate, iodate, vanadate, copper (II).

It should be noted that selenite, tellurite, vanadate, iodate, iron (III), copper (II) ions are only reduced in hydrochloric acid solutions, they are not reduced in sulfuric acid solutions. Here, presumably, the difference in the depolarizing effect of chloride and sulfate ions becomes apparent. Arsenate ions do not interact with mercury even in acid solutions.

The list of ions capable of being reduced by mercury, obviously, is not limited to the ions listed here. But even the small amount of experimental evidence given in Tables 1 and 2 is sufficient to indicate clearly the reactivity of mercury with respect to a whole series of ions. These results enable one to affirm that during polarography of the ions which we have studied, there will occur interaction between them and mercury with formation (in most cases) of sparingly soluble compounds. This interaction should lead to a drop in, and frequently even to complete disappearance of, the diffusion current of the materials being reduced. The true value of the reduction current is only attained at potentials at which oxidation of mercury ceases. In this connection, during the polarographic process one might expect the appearance of step-shaped waves even in the absence of a stepwise reduction of the materials being polarographed.

As an example of the participation of mercury in the reduction of metal ions by the amalgams of more-negative metals one can induce the reduction of copper by cadmium and amalgam.

In a previous study of this process, we established that copper is reduced by a cadmium amalgam ( 0,5% Cd) at a definite, almost constant, potential (−0,4 volt) to the metal. After a certain time interval there is observed a potential jump to positive values. After the potential jump the reduction process continues, but in this case univalent copper and not copper metal is formed. It might be assumed that in the reduction of copper to the univalent state only cadmium participates. But the results of experiments on the reduction of copper by mercury (Table 3) showed that mercury is capable, at a given potential value, of reducing copper in hydrochloric acid solutions. Analysis of the solution and precipitate formed during the cementation of copper by the amalgam, showed that mercury and cadmium at a given positive potential can simultaneously participate in the reduction of copper.

* On shaking a molybdate solution in a supporting electrolyte of KSCN and KI with mercury, the color of the solution changes to blue-green and blue, respectively. When no mercury is present this is not observed. We did not establish the extent of the reduction.

Simultaneous participation of mercury in the reduction reaction was also observed during the cementation of tellurium (IV) by a cadmium amalgam in hydrochloric acid solutions (Table 4). The yield of tellurium with respect to cadmium exceeded 100% as a result of its reduction not only by cadmium, but also by mercury. Under these conditions mercury reduced tellurium (IV) at negative potentials (−0.13 volt) (normal hydrogen electrode). As soon as all the cadmium had been removed from the amalgam, there was observed a steplike change in the potential of the amalgam to more positive values, but reduction of tellurium by mercury did not cease even at this positive potential value.

## SUMMARY

A study has been made of the reduction of a number of ions by metallic mercury in various solutions containing ions which can shift the potentials of the anodic oxidation of mercury.

It has been shown that permanganate and persulfate ions are reduced by mercury in neutral, alkaline, and acid solutions; iron (III) and molybdate in nonacidified and acid solution. Selenite, tellurite, vanadate, iodate, chromate, copper (II) are only reduced in acid solutions, a very strong effect on the reduction being displayed not only by the acidity of the solution, but also by the presence of other anions which shift the potential of the anodic oxidation of mercury.

The mercury potentials during the reductions have been measured. The value of the mercury potential depends on both the nature of the depolarizer and on the nature of the ion being reduced.

It has been shown that during the cementation of copper and tellurium by a cadmium amalgam, mercury participates simultaneously with the cadmium in the reduction reaction.

## LITERATURE CITED

[1] I. M. Kolthoff and J. J. Lingane, Polarography [Russian translation] (Moscow, 1948) p. 290.

[2] J. M. Issa, J. E. Khalafalla, and R. M. Issa, Rec. trav. chim. 75, 1031 (1956).

[3] E. P. Parry and M. G. Jakubik, Anal. Chem. 26, 129 (1954).

[4] Hahl Z. Filipovič, Z. Gasparac, and V. Klemenčič, J. Amer. Chem. Soc. 76, 2074 (1954).

[5] Ya. I. Tur'yan, Zhur. Fiz. Khim. 31, 2423 (1957).

[6] Ya. I. Tur'yan, Zhur. Anal. Khim. 11, 71 (1956).*

[7] K. Micka, Coll. Czechoslov. Chem. Comm. 21, 647 (1956).

[8] F. Paschen, Annalen der Physik u. Chemie, Neue Folge, No. 5, 36 (1890).

[9] J. Heyrovsky, Technique of Polarographic Investigation [Russian translation from Czech.] (IL, Moscow, 1951) p. 77.

[10] Noboyiki Tanaka and Teisuke Murayama, Z. physik. Chemie 11, 366 (1957).

[11] S. Wakkad, T. M. Salem, and S. Khalafalla, J. Chem. Soc. 1702 (1955).

[12] R. H. Cousens, D. Ives, and R. W. Pittman, J. Chem. Soc. 3972 (1953).

[13] R. H. Cousens, D. Ives, and R. W. Pittman, J. Chem. Soc. 3980 (1953).

[14] R. H. Cousens, D. Ives, and R. W. Pittman, J. Chem. Soc. 3988 (1953).

[15] R. B. Simpson, R. L. Evans, and H. A. Saroff, J. Amer. Chem. Soc. 77, 1483 (1955).

[16] P. Kivalo and H. A. Laitinen, J. Amer. Chem. Soc. 77, 5205 (1955).

[17] O. A. Songina and Z. B. Rozhdestvenskaya, Zhur. Anal. Khim. 11, 717 (1956).*

[18] T. A. Kryukova, Doklady Akad. Nauk SSSR 25, 517 (1949).

[19] A. N. Frunkin and G. M. Florianovich, Doklady Akad. Nauk SSSR 80, 907 (1951).

[20] F. P. Treadwell and V. T. Hall, Qualitative Analysis [Russian translation] (1946).

* Original Russian pagination. See C. B. Translation.

[21] N. H. Furman and W. M. Murray, J. Amer. Chem. Soc. 58, 429 (1936).

[22] N. H. Furman and W. M. Murray, J. Amer. Chem. Soc. 58, 1689 (1936).

[23] L. W. McCay and W. T. Anderson, J. Amer. Chem. Soc. 43, 2372 (1921).

[24] L. W. McCay and W. T. Anderson, J. Amer. Chem. Soc. 44, 1018 (1922).

[25] D. Borar, J. Chem. Soc. 99, 1414 (1911).

* Original Russian pagination. See C. B. Translation.

# THE USE OF STATIONARY MERCURY ELECTRODES IN OSCILLOGRAPHIC POLAROGRAPHY

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Oscillographic polarography permits the use of stationary electrodes for analytical purposes because of the short time it takes to record the current–voltage curves [1-2]. In such cases the value of the current is established very rapidly and is well reproduced. Polarographic maxima do not appear on the current–voltage curves in most cases, and it is therefore unnecessary to add surface-active materials to the solution. Dissolved oxygen does not distort the current–voltage curves, and reproducible results are obtained without removing oxygen from the test solution [3].

Some research workers [2, 4] have used a mercury pool as a cathode for the determination of materials at concentrations less than $10^{-5}$ M by oscillographic polarography. The determination was carried out in the absence of dissolved oxygen. Electrolysis on stationary electrodes in the presence of dissolved oxygen is of essential importance for the automatic control of plant streams. In this connection a series of experiments was carried out on the quantitative determination of certain elements in the presence of $O_2$. All the measurements were made on a GEOKhI oscillographic polarograph [5]. The peak potential ($\varphi_p$) and the half-peak potential ($\varphi_{p/2}$) are given relative to the saturated calomel electrode.

## Electrolysis of the Quiescent Liquid

The electrolytic cell (Fig. 1) which is an open glass cylinder (internal diameter 4.5 cm, height 2.5 cm) consisted of two stationary mercury electrodes. The polarizing electrode was mercury in a narrow tube with an internal diameter of 0.56 cm and 1.6 cm long, while the nonpolarized electrode was mercury in the wide part of the cylinder. The area of the mercury surface in the tube was approximately one fiftieth of the area of the mercury in the large cylinder. The inner glass cylinder was provided with four small holes for the inert gas to escape. The outer cylinder served as a water seal. In cases where oxygen was removed from the test solution, the cell was closed with a lid into which were fused a thin tube for passing through hydrogen, a calomel electrode, and a tube for an agar siphon. The calomel electrode was used for determining the potential of the polarizing mercury electrode.

The cell was mounted in a plastic beaker fitted with plugs. The plugs fitted into the socket of the setup connected to the apparatus by a coaxial wire.

In order to prevent the electrolyte from flowing between the mercury and the glass, the inner surface of the tube was covered with a thin film of silicone. The surface area of the mercury (S) was determined by means of a microscope and by comparing the currents on the stationary and dropping electrodes for the same concentration of material and under the same electrolysis conditions. It was almost constant for the same potential value.

A change in the curvature of the meniscus on changing the potential of the mercury leads to a movement of the solution and as a consequence the conditions of linear diffusion break down to some extent. In order to

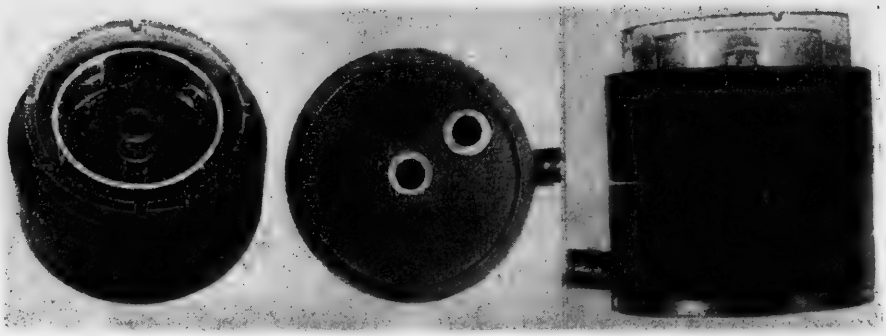

Fig. 1. Electrolytic cell consisting of two stationary mercury electrodes.

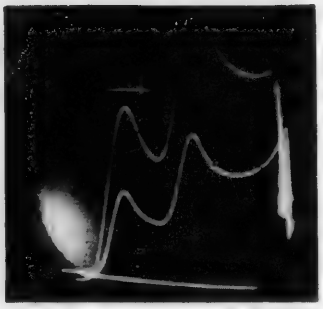

Fig. 2. Oscillogram of the anodic waves obtained at various concentrations of $Cd^{2+}$ and $Pb^{2+}$ in 1 N HCl on a stationary mercury electrode. $U_{=} = -1.0$ volt; $U_{\sim} = 0.944$ volt. The following are compared in the Fig.: supporting electrolyte 1 N HCl containing 27 μg $Cd^{2+}$/ml and 53 μg $Pb^{2+}$/ml – lower curve; and the current for the same medium to which has been added 65 μg $Cd^{2+}$/ml and 120 μg $Pb^{2+}$/ml – the upper curve. The straight line is the zero line. The upper curve is displaced slightly to the left and the peak for lead cannot be seen on it since it does not lie on the screen of the cathode ray tube.

avoid the effect of the curvature of the meniscus on the linear diffusion conditions it is necessary to increase the tube diameter to 2.0 cm; however, such a considerable increase in the surface area of the polarizing electrode would lead to a considerable increase in the cell dimensions on account of the increase in the area of the reference electrode. Such a huge cell is not always convenient in practice on account of the appreciable value of the capacity current. An indifferent electrolyte was poured into the electrolyzer. The original volume was 8 ml. To this was added dropwise from a buret a solution of a salt of the test element. After addition of each portion the test solution was electrolyzed at a definite time interval after mixing the solution, the rate (v) at which the potential was changed being −3.4 volt/sec. The curves given below were recorded 1 minute after mixing the solution, during one sweep with a 9 sec delay. Dissolved oxygen was not removed from the solution. The values for the maximum current ($I_p$) of the test ion are the values obtained after correcting for the increase in the original volume following from additions of the standard solution.

Quantitative determination of $Pb^{2+}$ and $Cd^{2+}$ in 1 N HCl.

The oscillogram of $Cd^{2+}$ and $Pb^{2+}$ in 1 N HCl (Fig. 2) was obtained during anodic polarization, when a constant negative potential ($U_{=} = -1.0$ volt) and a positive saw-toothed voltage ($U_{\sim} = 0.944$ volt) were applied to the cell.

Clearly defined anodic waves were observed on the oscillogram for Cd and Pb at values of $\varphi_p$ and $\varphi_{p/2}$ of −0.64 and −0.67 volt (for Cd) and of −0.38 and −0.41 volt (for Pb). The difference between $\varphi_p$ and $\varphi_{p/2}$ for the two elements is 0.03 volt, which is close to the theoretical value for reversible processes [6]. The calculation of the current of the second peak lead in this case, was carried out by means of the formula for the descending branch of the first wave ($Cd^{2+}$) for a reversible reaction [7].

The value of the current ($I_{reversible}$) on the descending branch of the first wave at a distance in excess of 2 volt from the first peak is determined by the relation:

$$I_{rever} = n_1 F S C_0 \sqrt{v} \sqrt{\frac{D}{\pi}} \sqrt{\frac{0,964}{(\varphi_1 - \varphi_2) + \frac{0,0056}{n_1}\left(\frac{T}{T_0}\right)}} \cdots \quad (1)$$

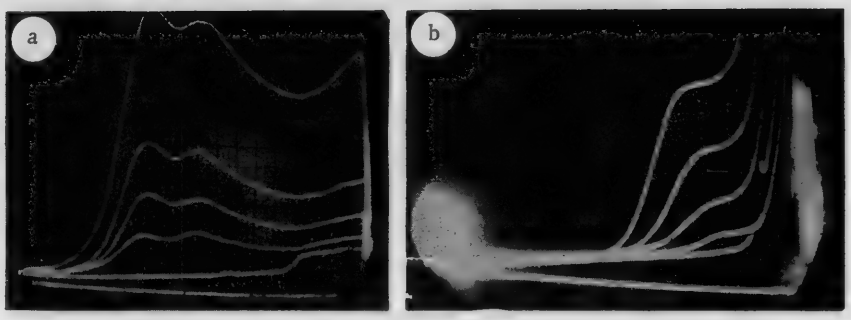


Fig. 3a. Oscillogram of the anodic waves of niobium in 23 N $H_2SO_4$ on a stationary mercury electrode. $U_{=} = -1.12$ volt; $U_{\sim} = 0.944$ volt.

Fig. 3b. Anodic current–voltage curves for various concentrations of $Ti^{IV}$ in 23 N $H_2SO_4$ on a stationary mercury electrode. $U_{=} = -0.78$ volt; $U_{\sim} = 0.944$ volt.

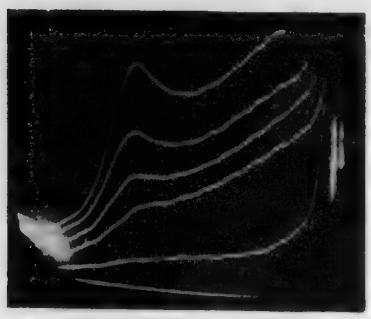

Fig. 4. Oscillogram for anodic waves of uranium in 1 N $HNO_3$ on a stationary mercury electrode. $U_{=} = -0.87$ volt; $U_{\sim} = 0.944$ volt.

Here $I_{reversible}$ is expressed in amps, S in $cm^2$, $C_0$ in mole/ml, D in $cm^2/sec$; $\varphi_1$ and $\varphi_2$ are the potentials at which the peaks of the first and second waves appear. $T = T_0 + t$; $T_0 = 273°$, F is the Faraday number; and $n_1$ is the number of electrons which participate in the electrochemical reaction.

By substituting in Eq. (1) the following values: S = = 0.386 $cm^2$; $C_0 = 2.42 \cdot 10^{-7}$ mole/ml, v = 3.4 volt/sec, $D_{Cd^{2+}} = 7.16 \cdot 10^{-6}$ $cm^2/sec$, $\varphi_1 - \varphi_2 = 0.26$ volt and T = = 298°, we find that $I_{reversible}$ for $\varphi_2 = -0.38$ volt is equal to 184 $\mu$a, which on Fig. 2 corresponds to the line opposite the lead peak. The maximum current of $Cd^{2+}$ on the lower curve is 336 $\mu$a. Thus, by means of the relation (1) it is possible to avoid the distortion of the second wave, while the true value of Ip for $Pb^{2+}$ becomes 408 instead of 377 $\mu$a. The error arising from the distortion of the lead wave does not exceed 8%. For 65 $\mu$g $Cd^{2+}$/ml the value of $I_p$ is 816 $\mu$a.

Quantitative determination of $Nb^V$ and $Ti^{IV}$ in 23 N $H_2SO_4$. A standard solution of $Nb^V$ and $Ti^{IV}$ in 23 N $H_2SO_4$ was prepared as before [8].

On the oscillogram (Fig. 3a) are shown the anodic waves for $Nb^V$ in 23 N $H_2SO_4$ at $U_{=} = -1.12$ volt and $U_{\sim} = 0.944$ volt. The lower straight line is the zero line, the current of the supporting electrolyte (23 N $H_2SO_4$). On the upper curves, niobium waves obtained at various concentrations of niobium are added to the supporting electrolyte current. The niobium $Nb^{III}$ peaks on the second, third, fourth, and fifth curves correspond to 125, 250, 385, and 770 $\mu$g Nb/ml. The following currents correspond to these concentrations: 138.7, 275.4, 428.4, and 856.8 $\mu$a. $\varphi_p$ $Nb^{III} = -0.41$ volt which is close to the value of the potential for the niobium peak obtained on a dropping mercury electrode [9]. S = 0.363 $cm^2$.

At a higher positive potential a scarcely observable peak appeared on the current–voltage curves. This, presumably is caused by adsorption of $Nb^{III}$ on the mercury surface. A similar peak is also observed on the anodic curves of niobium obtained on a dropping electrode [9].

In Fig. 3b are shown anodic current–voltage curves for various concentrations of $Ti^{IV}$ in 23 N $H_2SO_4$. $U_{=} = -0.78$ volt, $U_{\sim} = 0.944$ volt. The sweep of the saw-shaped impulse changed from $-0.78$ to $+0.164$ volt. On this oscillogram (Fig. 3b) a comparison is made of the current of the supporting electrolyte – 23 N $H_2SO_4$ – and of the same medium to which various amounts of Ti have been added. The lower, straight line is the zero line. It is clear from Fig. 3 that with increasing titanium concentration there is observed a displacement of the whole curve to more negative potential values. It amounts to 0.13 volt. Such a significant shift of the

TABLE 1

Simultaneous Determination of Ti and Nb in 23 N $H_2SO_4$

| Introduced into the solution | | $\frac{C_{Nb}}{C_{Ti}}$ | Found | | Error, % | |
|---|---|---|---|---|---|---|
| niobium, μg/ml | titanium, μg/ml | | niobium, μg/ml | titanium, μg/ml | niobium | titanium |
| 38,0 | 304 | 0,125 | 39,4 | 299 | +3,7 | −1,7 |
| 50,0 | 100 | 0,5 | 52,4 | 98,6 | +4,8 | −1,4 |
| 125 | 83 | ~1,5 | 121,4 | 84,8 | −2,9 | +2,2 |
| 100 | 25 | 4,0 | 96,8 | 26,0 | −3,2 | +4,0 |
| 390 | 65 | 6,0 | 396,0 | 63,2 | +1,5 | −2,8 |

TABLE 2

Relation Between Current and Uranium Concentration in 1 N $HNO_3$

| Uranium, μg ml | $I_p$, μa | | Uranium μg ml | $I_p$, μa | |
|---|---|---|---|---|---|
| | anodic polarization, $U_= -0.87$ v $U_\sim$ 0.944 v | Cathodic polarization $U_= -0.1$ v, $U_\sim$ 0.944 v | | anodic polarization, $U_= -0.87$ v $U_\sim$ 0.944 v | Cathodic polarization $U_= -0.1$ v, $U_\sim$ 0.944 v |
| 30 | 20,4 | — | 416 | 282,9 | — |
| 60 | 40,8 | — | 480 | 315,8 | 342,0 |
| 120 | 81,6 | 89,5 | 960 | — | 689,0 |
| 240 | 158,6 | 177,7 | 1920 | — | 1364,0 |

TABLE 3

Relation Between Current and $Cd^{2+}$ Concentration in 1 N HCl in a Flowing Cell. Anodic Polarization. $U_= = -0.9$ volt; $U_\sim = 0.944$ volt.

| $Cd^{2+}$, μg/ml | On fresh mercury surface | | On the same mercury surface which was not changed for: | | | |
|---|---|---|---|---|---|---|
| | | | 12 hours | | 24 hours | |
| | $I_p$, μa | $I_{0,30}$, μa | $I_p$, μa | $I_{0,30}$, μa | $I_p$, μa | $I_{0,30}$, μa |
| 0,1 | 0,54 | — | 0,52 | — | 0,55 | — |
| 0,2 | 1,04 | — | 1,06 | — | 1,05 | — |
| 0,3 | 1,53 | 0,74 | 1,55 | 0,76 | 1,58 | 0,77 |
| 0,4 | 2,14 | 1,01 | 2,18 | 1,03 | 2,15 | 1,02 |
| 0,5 | 2,69 | 1,23 | 2,64 | 1,22 | 2,73 | 1,25 |
| 1,5 | 8,12 | 3,58 | 8,05 | 3,51 | 8,17 | 3,61 |
| 2,5 | 13,43 | 6,15 | 13,56 | 6,28 | 13,49 | 6,21 |
| 6,0 | 32,54 | 14,46 | 32,32 | 14,24 | 32,68 | 14,39 |
| 10,0 | 56,00 | 23,52 | 54,89 | 22,80 | 55,11 | 23,20 |
| 20,0 | 108,40 | 47,92 | 110,50 | 49,25 | 110,20 | 48,25 |
| 40,0 | 220,00 | 93,51 | 217,50 | 91,52 | 224,09 | 94,02 |
| 50,0 | 283,00 | 117,52 | 275,30 | 109,82 | 279,20 | 111,41 |

curve cannot be related to an ohmic drop in potential, which in the given instance amounts to not more than 0.006 volt. It can be explained by the interaction of the anodic waves of $Ti^{III}$ with the capacity current of the supporting electrolyte. Peaks for $Ti^{III}$ are absent on the curve. However, when the capacity current is subtracted from the anodic waves of titanium, then a distinct $Ti^{III}$ peak is observed at $\varphi_p = +0.16$ volt on the current–voltage curve, which indicates that the electrode reaction $Ti^{III} \rightarrow Ti^{IV}$ approximates to a reversible reaction.

For analytical purposes the method adopted was to measure from the capacity current, taken in the absence of $Ti^{IV}$, to the break on the anodic wave of titanium. Such an approximate measurement of the anodic

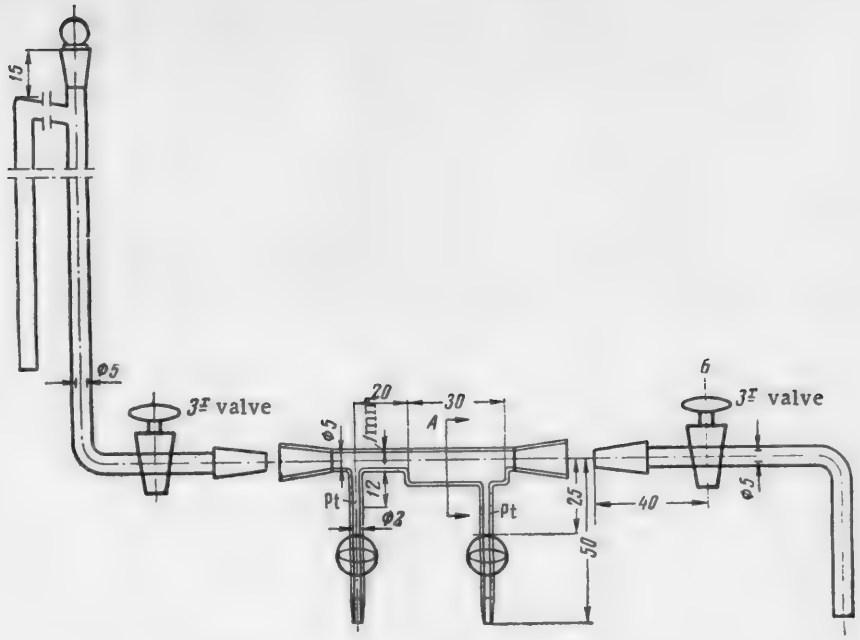


Fig. 5. Cell for analysis of plant streams.

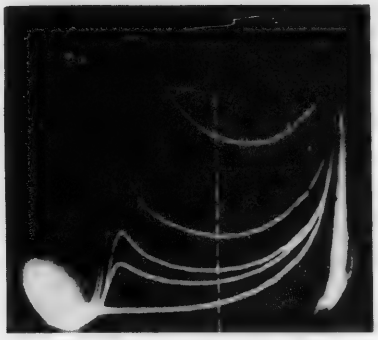

Fig. 6. Anodic current–voltage curves for various concentrations of $Cd^{2+}$ in 1 N HCl in a flowing cell. $U_{=} = -0.9$ volt; $U_{\sim} = 0.944$ volt.

current of titanium preserves its proportionality to concentration, as can be seen from the oscillograms adduced (Fig. 3b). The Ti waves on the second, third, fourth, and fifth curves correspond, respectively, to 25, 65, 131, and 220 μg Ti/ml. The currents corresponding to these concentrations are 61.2, 163.2, 326.4, and 540.6 μa.

The difference of 0.6 volt between the potentials of the Nb and Ti peaks in 23 N $H_2SO_4$ indicates that it should be possible to determine these elements simultaneously. Results for the quantitative determination of $Ti^{IV}$ and $Nb^{V}$ in each other's presence on the basis of the anodic waves in 23 N $H_2SO_4$ are given in Table 1. The results given in Table 1 show that the deviation observed between the amounts taken and the amounts found, does not exceed the error usually obtained with a dropping mercury electrode.

Quantitative determination of $U^{VI}$ in 1 N $HNO_3$. The oscillogram for $UO_2^{2+}$ (Fig. 4) was obtained during anodic polarization, when $U_{=} = -0.87$ volt and $U_{\sim} = 0.944$ volt were applied to the electrolytic cell. On this curve a comparison is made of: the current of the supporting electrolyte 1 N $HNO_3$ – the first curve below, and the current of solutions containing various amounts of U – the top curves. The current–voltage curves are displaced relative to each other in a vertical direction. Curves 2, 3, 4, and 5 correspond, respectively, to 30, 60, 120, and 240 μg U/ml. The lower straight line is the zero line. Distinct anodic waves for quinquevalent uranium are observed on the current–voltage curves at $\varphi_p = -0.14$ volt. The values of $I_p$ on the oscillogram in Fig. 4 and the results of other experiments are given in Table 2.

From the results given in Table 2 it is clear that the cathodic waves of sexivalent uranium are 8-12% higher than the anodic waves of quinquevalent uranium. Both the anodic and cathodic waves of uranium are linearly related to its concentration.

Numerous experiments which we have carried out show that the stable value of the current on a stationary mercury electrode is established rapidly (thanks to the short time taken to record the current–voltage curves)

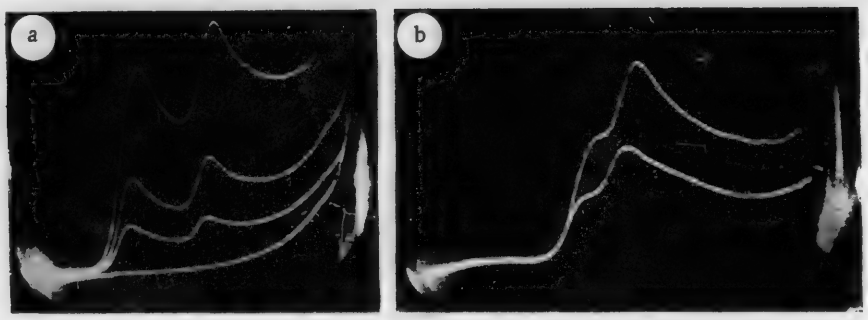


Fig. 7a. Oscillogram of anodic waves of $Cd^{2+}$ and $Pb^{2+}$ in 1 N HCl in a flowing cell. $U_{=} = -0.9$ volt; $U_{\sim} = 0.944$ volt.

Fig. 7b. Anodic current–voltage curves for $Cd^{2+}$ and $In^{3+}$ in 1 N HCl in a flowing cell. $U_{=} = -1.0$ volt; $U_{\sim} = 0.944$ volt.

and is readily reproduced. This fact is of essential significance for the automatic control of technological streams (plant streams).

## Electrolysis of Flowing Solutions

Lewis and Overton [10], Bertram, Lerner, Petretic, Roszkowski, and Rodden [11], Alkire, Koyama, Hahn, and Michelson [12] have used a polarographic method for the continuous determination of uranium in flowing, dilute, technical solutions and in discarded, radioactive plant streams.

The use of a dropping mercury electrode is bound up with difficulties arising from the accumulation of a large amount of mercury contaminated with radioactive materials, the necessity of removing dissolved oxygen by means of an inert gas, the addition of surface-active materials to the test solution, and the presence of oscillations on the polarogram. It is impossible to suppress the oscillations on the polarograms significantly by using electrolytic condensers in parallel with the resistive load and the cell, when plant streams are being analyzed. The presence of oscillation leads to a decrease in the experimental accuracy of a determination. When a dropping electrode is used, it is necessary during the time the current–voltage curve is being recorded, that the test solution should be stationary for at least 2-3 minutes. This necessitates the introduction of an additional apparatus in the automatic line. The capillary which is immersed for a long time in an aggressive medium, e.g., in $HNO_3$, sucks the liquid inside, as a result of which its dropping period alters with time, leading to nonreproducible results. The use of a rubber tube also leads to contamination of the capillary, so that it has to be changed often.

In view of the drawbacks listed above which are associated with ordinary and derivative polarography for the continuous analysis of plant streams, it was deemed expedient to use oscillographic polarography for this purpose.

In Fig. 5 is shown an electrolytic cell for the analysis of plant streams in which mercury in a capillary with an internal diameter of 0.20 cm serves as the polarizing electrode. The large surface of the mercury in the convex part of the tube serves as the nonpolarizing electrode. The test solution was introduced into the cell either by means of a siphon or by a pressure difference at two points. The polarograms were taken without stopping the liquid. Linear voltage impulses were applied to the cell at 9 sec intervals at a rate of V = 3.4 volt/sec. An aliquot of the test element was added to 1 liter of indifferent electrolyte. After each addition of aliquot to the supporting electrolyte the test solution was passed several times through the cell at the rate of 258 ml/sec, only then was the oscillogram photographed. Dissolved oxygen was not removed from the solution. The mercury surface was not renewed for a long time. For repeated determination of the same concentration of the test element, the cell was carefully washed by passing indifferent electrolyte through it after each series of experiments. In order to prevent penetration of electrolyte between the mercury and the glass, the internal surface of the cathode compartment was smeared with silicone. The area of the electrode was determined by comparing the currents for the same concentration of the material under the same electrolysis conditions in the "flowing" cell and on the dropping mercury electrode.

TABLE 4

Relation Between the Maximum Current of $Cd^{2+}$ and $Pb^{2+}$ and Their Concentration in 1 N HCl in a Flowing Cell. Anodic Polarization $U_{=} = -0.9$ volt; $U_{\sim} = 0.944$ volt. The Mercury Surface was not Renewed for 26 Hours

| $Cd^{2+}$ concentration, μg/ml | $I_p$, $Cd^{2+}$, μa | $Pb^{2+}$ concentration, μg/ml | Approximate value of $I_p$ for $Pb^{2+}$, μa | True value of $I_p$ for $Pb^{2+}$, calculated by means of modified formula (1), μa |
|---|---|---|---|---|
| 0,5 | 2,71 | 0,5 | 1,49 | 1,59 |
| 1,5 | 8,28 | 1,5 | 4,39 | 4,68 |
| 6,0 | 33,90 | 6,0 | 17,98 | 18,73 |
| 12,0 | 67,80 | 12,0 | 35,96 | 37,67 |
| 24,0 | 139,20 | 24,0 | 71,42 | 77,23 |

Below are shown a series of oscillograms obtained in the flowing cell in which the diameter of the polarizing mercury electrode was 0.27 cm.

Quantitative determination of cadmium in 1 N HCl. In the oscillogram in Fig. 6 obtained during anodic polarization ($U_{=} -0.9$ volt and $U_{\sim} = 0.944$ volt) a comparison is made of the supporting electrolyte (1 N HCl) current, – the first curve on the bottom – and of the same medium to which had been added various amounts of $Cd^{2+}$ – the upper curves. The sweep of the saw-shaped voltage changes from −0.9 volt to +0.044 volt. Clear-cut $Cd^{2+}$ peaks are observed on the current–voltage curves, with the exception of the upper peak, which does not lie on the screen of the cathode ray tube. The ohmic potential drop does not exceed 0.006 volt, since $\varphi_p$ is displaced insignificantly to more positive potential value for various $Cd^{2+}$ concentrations.

Curves 2, 3, 4, and 5 correspond, respectively, to: 6.0, 10.0, 20, and 50 μg $Cd^{2+}$/ml. The following values of $I_p$ correspond to these concentrations: 32.54, 56.0, 108.4, and 283.0 μa.

The concentration of the test element can also be determined from the current of the descending branch of the polarographic waves at a distance greater than 0.2 volt from the peak, as follows from the equations given below which are derived from a stationary liquid [7]. The following values were obtained for the current at distances of 0.20, 0.27, 0.30 volt from the maximum:

$$\left.\begin{aligned} I_{0.20} &= 1{,}143 \cdot 10^5 \cdot n_1 S C_0 \sqrt{D}\sqrt{V} \\ I_{0.27} &= 1{,}000 \cdot 10^5 \cdot n_1 S C_0 \sqrt{D}\sqrt{V} \\ I_{0.30} &= 0{,}942 \cdot 10^5 \cdot n_1 S C_0 \sqrt{D}\sqrt{V} \end{aligned}\right\} . \qquad (2)$$

The values of the current (I) at a distance of 0.3 volt from the peak are determined in Fig. 6. The corresponding points on the curves are marked by the dotted line. The following values were found for the same $Cd^{2+}$ concentration: 14.46, 23.52, 47.92, and 117.52 μa.

A comparison of the value found for I, with the theoretical values calculated by means of formula (2) for 10 μg $Cd^{2+}$/ml, shows that the deviation between the two values amounts to 20% (S = 0.194 $cm^2$ and $I_{0.30}$ = = 18.04 μa instead of 23.52 μa). This significant difference between the experimentally determined current and the theoretically calculated value is caused by the flow of the liquid. Despite such a significant deviation, the oscillogram in Fig. 6 shows that in the flowing liquid, the current of the descending branch of the wave is linearly proportional to the cadmium content of the solution.

Table 3 contains results for the determination of $Cd^{2+}$ in 1 N HCl; they were obtained on fresh mercury and on mercury whose surface had not been renewed.

It is clear from the results given in Table 3 that the anodic waves for cadmium measured on the basis of the peak height of the descending branch of the wave, are directly proportional to the concentration, both on a fresh mercury surface and on the surface of mercury which had been subjected to prolonged electrolysis.

Quantitative determination of $Pb^{2+}$, $Cd^{2+}$, and $In^{3+}$ in 1 N HCl. On the oscillogram in Fig. 7a are shown anodic curves for various concentrations of $Cd^{2+}$ and $Pb^{2+}$ in 1 N HCl for $U_{=} = -0.9$ volt and $U_{\sim} = 0.944$ volt. The potential sweep alters from −0.9 volt to +0.044 volt. The first curve from below is the current of the supporting electrolyte − 1 N HCl. Cd and Pb waves are added to the supporting electrolyte current on the upper curves. The first peak on the left corresponds to $Cd^{2+}$, while the second corresponds to $Pb^{2+}$. $\varphi_P Cd = -0.64$ volt; $\varphi_P Pb = -0.38$ volt. The coincidence of the peak potentials of cadmium and lead with $\varphi_P Cd^{2+}$ and $Pb^{2+}$ on a dropping and on stationary electrodes shows that electrolysis in a flowing cell does not distort the nature of the current−voltage curves (compare Figs. 2 and 7a). The oscillogram in Fig. 7a was obtained on the same mercury surface as that used for Fig. 6, but it was not renewed for 26 hours in the course of a given series of experiments. The Cd and Pb peaks on curves 2, 3, and 4 were taken for a solution of 1 N HCl containing, respectively, 6, 12, and 24 μg of $Cd^{2+}$ and $Pb^{2+}$/ml. The following values of $I_P$ were obtained for Cd: 33.90, 67.80, and 139.2 μa. Although the mercury surface was not renewed for a long time, the coincidence observed between the values of the maximum current of $Cd^{2+}$ with $I_P Cd$ in the absence of Pb (see Table 3) testifies to the good reproducibility of the results.

Measurements of the maximum current of Pb in Fig. 7a, starting from the minimum on the ascending curve to the peak, gave the following values of $I_P$ for concentrations of 6, 12, and 24 μg $Pb^{2+}$/ml: 17.98, 35.96, and 71.42 μa. Although such a measurement technique does not take into account distortion of the Pb wave by the preceding Cd wave, and does not give the true value of the current, it is nevertheless suitable for analytical purposes, since a linear relationship is observed between the current and the $Pb^{2+}$ concentration. The true values of $I_P$ should be 5-8% higher than the values given above.

Results for the simultaneous determination of $Cd^{2+}$ and $Pb^{2+}$ in 1 N HCl are given in Table 4. It follows from these results that it is possible to carry out a quantitative determination of Cd and Pb in a flowing cell, since the currents for $Pb^{2+}$ and $Cd^{2+}$ are linearly proportional to the concentrations. The lead content of the test solution can be evaluated by measuring the peak height from the level of the minimum preceding it.

Figure 7b, which was obtained during anodic polarization ($U_{=} = 1.0$ volt, $U_{\sim} = 0.944$ volt), shows that the flowing cell is also suitable for the simultaneous determination of In and Cd in 1 N HCl. The first wave from the left corresponds to $Cd^{2+}$, while the second corresponds to $In^{3+}$. Because of the proximity of the half-wave potentials of Cd and In in 1 N HCl, the $In^{3+}$ peak on the current−voltage curves is distorted by the preceding $Cd^{2+}$ wave. However, this does not interfere with the quantitative determination of indium, as long as the $In^{3+}$ content of the solution is evaluated by measuring the peak height from the level of the break preceding it on the curve. The lower curve was taken with 1 N HCl containing 5 μg $Cd^{2+}$/ml and 6.5 μg $In^{3+}$/ml. $I_P Cd^{2+} = 28.08$ μa; $I_P In^{3+} = 21.21$ μa. The upper curve was obtained for the same medium to which had been added 10 μg $Cd^{2+}$/ml and 10.5 μg $In^{3+}$/ml. For these concentrations of Cd and In the corresponding values of $I_P$ were 56.16 and 34.32 μA.

Quantitative determination of uranium in the presence of $Fe^{3+}$. The oscillogram for $U^{V}$ in Fig. 8 was obtained during anodic polarization ($U_{=} = -1.0$ volt, $U_{\sim} = 0.944$ volt) on a mercury surface which had been in contact with 1 N $HNO_3$ for a long time (96 hours). The following curves are compared on this Fig.: the current of the supporting electrolyte − 1 N $HNO_3$ − the first curve from the bottom, and the current for a solution containing various amounts of $U^{VI}$ and $Fe^{3+}$ − the upper curves. The ratio of Fe to U is 3.

The current−voltage curves are artificially shifted relative to one another in a vertical direction, and, in addition, the two upper curves are shifted slightly to the left. The bottom line is the zero line. A wave resulting from the presence of Hg ions in 1 N $HNO_3$ appears on the current of the supporting electrolyte. It almost coincides with the U wave. Accordingly, measurement of the peak heights of uranium in the given case was carried out from the level of the supporting electrolyte wave. Curves 2, 3, and 4 correspond to 58.4, 116.8, and 233.6 μg/ml. For these U concentrations the following values were obtained for $I_P$: 13.44, 25.76, and 51.80 μa. A series of experiments was carried out on the determination of U in the presence of $Fe^{3+}$: the concentrations of the latter are considerably higher than the concentration of $U^{VI}$ in the test solution. Results of the measurements of the peak heights are given in Table 5.

It is clear from the results given in Table 5 that the anodic currents of U are linearly proportional to its concentration both on a fresh mercury surface and on a mercury surface which has been in contact with the test solution for a long time. The presence of iron in the test solution in an amount which is four times the uranium concentration, does not interfere with the quantitative determination of the latter.

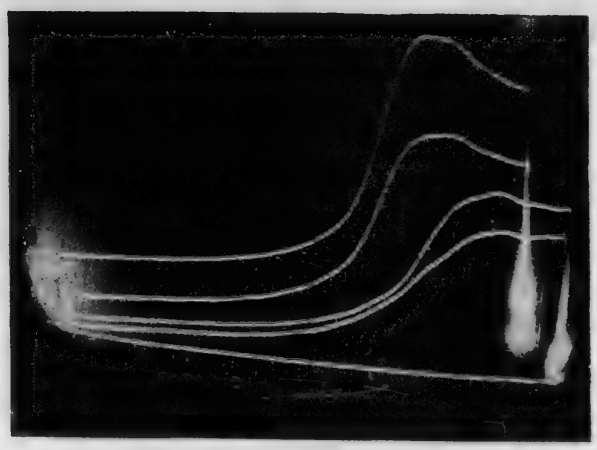

Fig. 8. Anodic curves for uranium in 1 N $HNO_3$ containing $Fe^{3+}$ in a flowing cell. $U_{=} = -1.0$ volt, $U_{\sim} = 0.944$ volt.

TABLE 5

Relation Between the Maximum Current and U Concentration in 1 N $HNO_3$ in a Flowing Cell in the Absence and in the Presence of $Fe^{3+}$

| On a fresh mercury surface | | | On a mercury surface which has not been renewed for 96 hours | | |
|---|---|---|---|---|---|
| U, μg/ml | Fe/U | $I_p$, μa | U, μg/ml | Fe/U | $I_p$, μa |
| 250 | 0 | 57,5 | 152 | 0 | 35,0 |
| 400 | 0 | 87,5 | 196 | 4 | 45,0 |
| 430 | 3 | 97,5 | 261 | 4 | 60,0 |
| 750 | 0 | 169,3 | 353 | 3 | 81,2 |
| 1050 | 2 | 230,8 | 522 | 4 | 120,0 |
| 1430 | | 325,9 | | | |

## SUMMARY

Oscillographic polarography can be used for the automatic control of production solutions; it possesses high sensitivity and selectivity, and the results obtained are reproducible.

## LITERATURE CITED

[1] P. Delahay, New Apparatus and Methods in Electrochemistry [Russian translation] (IL, Moscow, 1957) p. 69.

[2] R. C. Rooney, Talanta 2, 190 (1959).

[3] Ya. P. Gokhshtein, Zhur. Anal. Khim. 13, 36 (1958).*

[4] C. A. Streuli and W. D. Cooke, Analyt. Chem. 25, 1691 (1953); J. Phys. Chem. 57, 824 (1953); D. J. Roste, Analyt. Chem. 27, 1360 (1955); I. G. Nickelly and W. D. Cooke, Analyt. Chem. 29, 983 (1957).

[5] Ya. P. Gokhshtein, S. V. Kuz'min, A. F. Volkov, and V. A. Yanchevskii, Byull. Fil. Vsesoyuz. Inst. Nauch. i Tekhnich. Informatsii, Tema No. 39, p. no. 58-172/15 (1958); Zavodskaya Lab. 25, 1008 (1959).

[6] H. Matsuda and I. Ayabe, Z. Elektrochemie 59, 494 (1955).

* Original Russian pagination. See C. B. Translation.

[7] Ya. P. Gokhshtein and A. Ya. Gokhshtein, Doklady Akad. Nauk SSSR 128, 985 (1959);* Zhur. Fiz. Khim. 34, 7 (1960); Report given at a Conference on Polarographic Analysis held at Kishinev (October, 1959); Report given at the All-Union Conference on the Analysis of Rare and Semiconducting Elements, Moscow (December, 1959).

[8] Ya. P. Gokhshtein, Zavodskaya Lab. 22, 38 (1956).

[9] Ya. P. Gokhshtein, L. A. Genkina, and A. M. Demkin, Zavodskaya Lab. 25, 1042 (1959).

[10] I. A. Lewis and K. C. Overton, Analys. 79, 293 (1954).

[11] H. W. Bertram, M. W. Lerner, G. I. Petretic, E. S. Roszkowski, and C. I. Rodden, Analyt. Chem. 30, 354 (1958).

[12] G. I. Alkire, K. Koyama, K. I. Hahn, and C. E. Michelson, Analyt. Chem. 30, 1912 (1958).

* Original Russian pagination. See C. B. Translation.

# THE USE OF A "SOUNDING" ARC FOR FOLLOWING THE PASSAGE OF MATERIAL INTO DC ARC PLASMA

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The reproducibility of the results of the spectrographic determination of elements depends to a large extent on variations in the operational conditions of the spectrum excitation source, and on sporadic changes in the conditions under which the elements pass from the sample into the source plasma. Meanwhile, when an analysis is carried out, even when the electrical parameters of the arc (current strength and voltage) are kept strictly constant, the variations mentioned above in the conditions of the evaporation of the elements from the sample and their excitation in the plasma still remain without reliable control, and, accordingly, they cannot be taken into account during an evaluation of the accuracy of the results obtained.

In order to control the passage of the elements into the arc plasma, Rusanov [1] suggested a method based on measuring the potential difference at the ends of the source electrodes.

In the work described here an attempt was made to solve this problem by another method – by supplementing existing excitation sources (e.g., a dc arc) by a setup which would react more or less sensitively to changes in the conditions of the passage of the elements into the plasma, and would allow these processes to be followed by means of the simplest, e.g., sonic signal. Such a "sounding" arc [2] would open up a way for a more accurate experimental study of the processes occurring in the source, and its use in spectrographic practice would favor an increase in the reproducibility and accuracy of the analysis.

The present article includes some results obtained recently which illustrate the possibility of using a "sounding" arc for following the passage of material into the source plasma.

A schematic diagram of the source is shown in Fig. 1. To a dc arc is connected an oscillating circuit, the natural frequency period of which $T = 2\pi\sqrt{LC}$ lies within the range $2 \cdot 10^{-2}$ to $5 \cdot 10^{-5}$ sec. Accordingly, the vibrations of the plasma with this period are strengthened and appear externally in the "sounding" arc, which can be picked up aurally or recorded and analyzed quantitatively by means of an oscillograph, magnitophone, or a sound generator. In order that the ac component of the arc current is not branched into the main circuit, a high frequency choke is included in the "sounding" circuit. In order to increase the sounding power of the arc, an additional capacity C' is connected in parallel with the arc. In the circuit which we used in the work described here the self-inductance L was varied within the range 0.1 to 0.25 mH, while the capacities C and C' were varied within the limits 8 to 18 and 5 to 16 μF, respectively. The sounding intensity of the arc was measured by means of the cathode voltmeter of the sonic generator.

In order to increase the accuracy of the measurements of the duration and intensity of the sounding of the arc during an analysis, it was recorded on a magnetic tape. Such a technique is particularly effective for measuring very short time breakdowns in the conditions of the "sounding" source. It allows one to record and measure

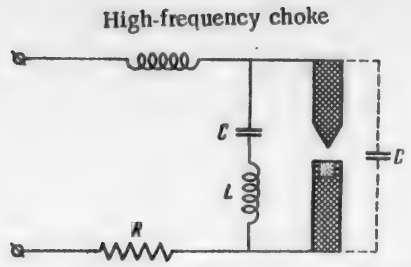


Fig. 1. Schematic diagram of a "sounding" arc.

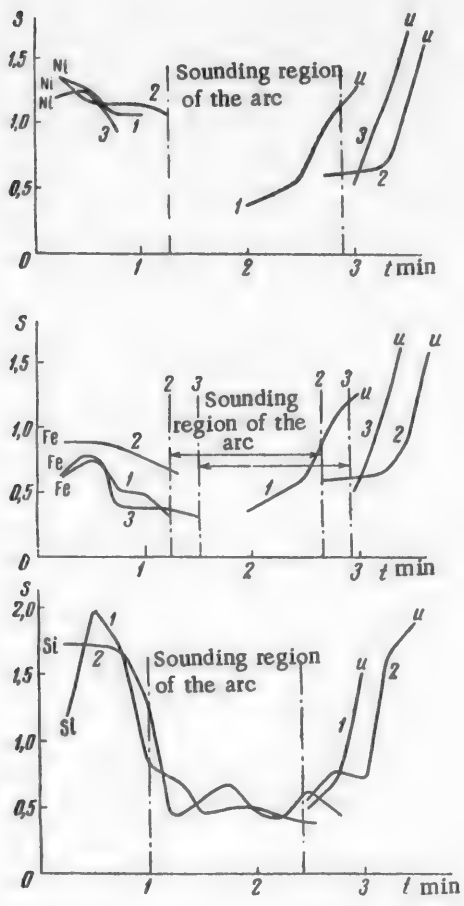


Fig. 2. Blackening-changing curves for the lines of nickel (at the top), iron (in the middle), and silicon (below) during their evaporation from uranoso uranic oxide on the cathode of a dc arc under ordinary conditions (1) and under the "sounding" conditions of the arc, for two values of the self-inductance L = 0.1 mH (2) and 0.25 mH (3).

reliably the breaks in the sounding of the arc of the order of fractions of a second. The use of such a magnetic recording may also prove useful for synchronous "scoring" of the matching frames during kinematographic recording of processes occurring in the arc plasma with time.

In order to illustrate some of the characteristics of a "sounding" arc, let us consider for example the evaporation of Fe, Ni, Si, and Al from uranoso uranic oxide in the presence of $Ga_2O_3$ and NaCl, which often, for various reasons, may occur in the sample being tested during analysis. For convenience in carrying out the experiments described (increasing the evaporation time of the impurities from difficultly volatile bases) the sample was not evaporated on the anode, but on the cathode of a dc arc from a crater 4 mm deep. The current was 12 amp. In Fig. 2 a comparison is made of the curves for changes in the blackening of the analytical lines Ni, Fe, and Si with time, during evaporation of these impurities from uranoso uranic oxide in a dc arc under ordinary conditions (before switching on the "sounding" circuit) and under the "sounding" conditions of the arc at two different values of the self-inductance. The dotted lines on the diagrams mark out the "sounding" region of the arc. As is evident, under the experimental conditions chosen the arc sounds in the time intervals following the almost complete evaporation of Fe and Ni from the sample, and precedes the intensive passage of the difficultly volatile base into the plasma. On going from the ordinary arc to a "sounding" arc there is observed a small additional hold up* during the passage of uranium into the arc, the magnitude of this hold-up being dependent on the value of the self-inductance of the oscillating circuit. The latter value also affects the shape of the evaporation curve of the element. Both these effects are manifested fairly clearly on the evaporation curves of Ni and Fe, and is much less clearly manifested on the curves relating to Si. Thus, in the case considered, the use of a "sounding" arc leads to a small extension of the interval separating the region of intense evaporation of the test impurities and the base from the sample, and also permits objective control (from the sound) during the analysis, of the time of evaporation of the main mass of nickel and iron from the test sample.

As experiments have shown, a "sounding" arc also permits one to fix accidental breakdowns in the normal passage of the elements – impurities into the source plasma, which may occur during the analysis of actual samples. Proof of this may be obtained by

* One of the reasons for this phenomenon may be a small decrease in the source temperature during the "sounding" period of the arc, which, as an approximate evaluation showed, may be 200-300°.

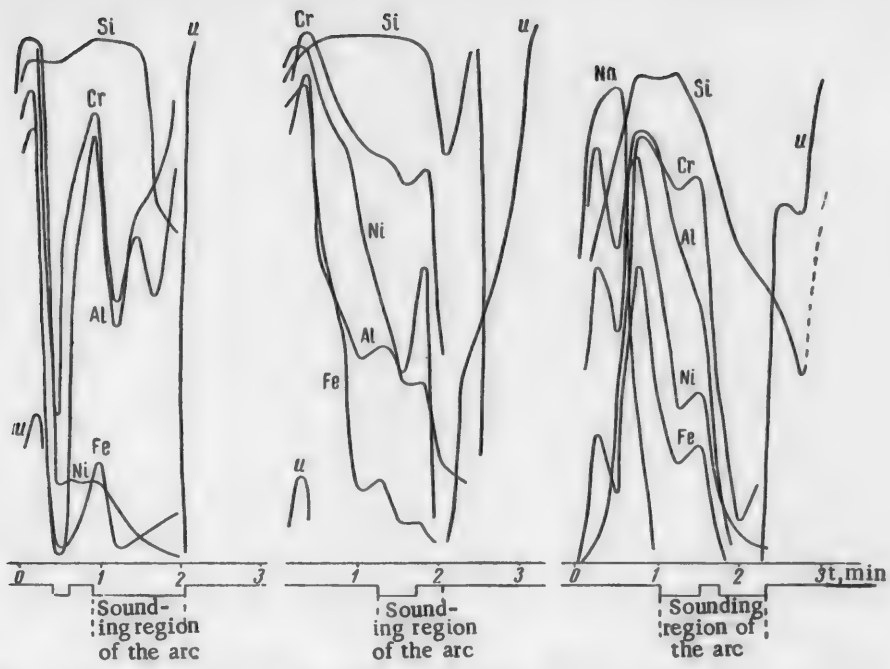


Fig. 3. Curves of the changes in blackening of the lines of Fe, Al, Ni, Cr, Si, and Na during the evaporation of these elements from various samples of uranoso uranic oxide on the cathode of a "sounding" arc. Below is shown graphically the character of the "sounding" arc during the experiment. The dotted lines mark out the "sounding region" during normal evaporation of impurities.

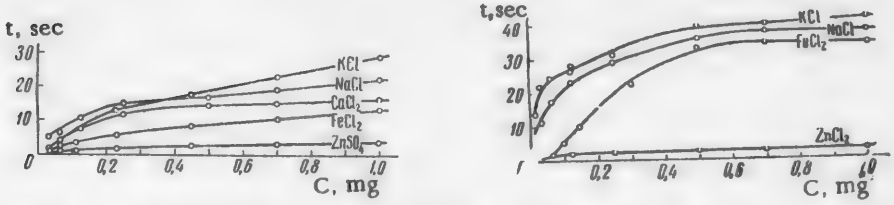


Fig. 4. The relation between the silent time of the "sounding" arc (t) and the content of various elements (C) evaporating from the anode (on the left) and the cathode (on the right) of the source.

considering Fig. 3,in which a comparison is made of the curves for changes in blackening of the analytical lines of the impurities and of uranium, obtained during evaporation of the elements from various samples, with the curve of a sounding arc during an experiment. It is clear that both the accidental holdup in the evaporation of Al, Ni, Cr, and Fe which occurs during an experiment, and to which the curves in Fig. 3 (on the left) relate, and the sudden increase in the content of all or some of these elements in the plasma, which occurs after evaporation of the main mass of impurities in the two other cases ( Fig. 3 in the middle and on the right), can be equally clearly recorded by means of a "sounding" arc. In the first case the arc starts to sound unexpectedly, while in the other two cases—on the contrary—there are observed more or less continuous pauses which are timed to the region of the "sounding" source. In practice this enables the analytical technique to be improved by two methods. It is possible to choose the exposure time for the spectrograms "by sound," and in this way factually take into account the characteristics of the passage of the test elements into the source plasma during the analysis of an actual sample. When a constant exposure time is used, the use of a "sounding" arc allows one to exclude from consideration (on the basis of experimental results) the results of measurements of those

TABLE

| Compound | Ionization potential of the atoms of the element, E (ev) | Mean temperature of the source plasma T (°K) | Duration of pause during evaporation from the anode (t, sec) |
|---|---|---|---|
| KCl | 4,3 | 4100 | 28 |
| NaCl | 5,0 | 4300 | 19 |
| Al (Metal) | 5,9 | 4600 | 18 |
| $Al_2O_3$ | 5,9 | 4600 | 28 |
| $CaCl_2$ | 6,2 | 4800 | 16 |
| $FeCl_3$ | 7,8 | 5300 | 14 |
| $SiO_2$ | 8,1 | 5500 | 13 |
| $ZnCl_2$ | 9,4 | 6200 | 3 |

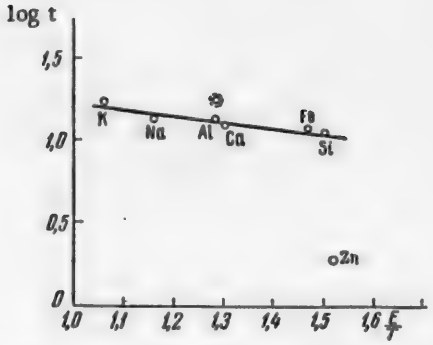


Fig. 5. Relation between log t and E/T during the evaporation of the same amount (1 mg) of various elements on the anode of a "sounding" arc. The dot surrounded by dashes belongs to $Al_2O_3$.

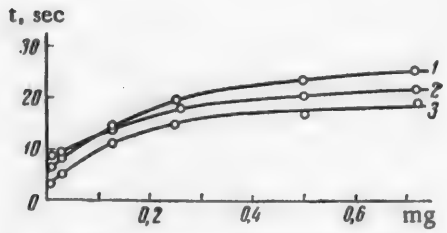


Fig. 6. Relation between the silent time of the arc (t) and the concentration of the impurity (C) during evaporation of sodium chloride from the surface of an anode (3) and from the crater of the electrode at a depth of 5 mm (2) and 7 mm (1).

spectrograms in the preparation of which there were observed appreciable breakdowns of the normal "sounding conditions" of the source for the test samples. In both cases, the use of a "sounding" arc will obviously favor an increase in the reproducibility and reliability of the results of spectrographic determinations.

In a series of special experiments an attempt was made to study systematically the properties of a "sounding" arc and to relate the basic parameters characterizing its operation – the intensity and duration of the sound signals or pauses – to the concentrations of the impurities evaporating on the electrode, their volatility, the values of the ionization potential of the atoms, the mean temperature of the source, the intensity of diffusion processes on the electrode and the nature of the bonds between the impurity atoms and the crystal lattice of the main material, and other factors. In order to simplify the experiments and for greater accuracy in determining the source temperature, the impurities were introduced directly into the carbon electrode. Under such conditions, in one series of experiments, in which was borne in view reduction to a minimum of the influence of effects determined by differences in the volatility of the elements, and the exclusion of the effect of diffusion processes on the electrode, solutions of the corresponding salts of the various elements (mainly as chlorides) were placed on the flat face of one of the electrodes of a dc arc (this face was treated beforehand with polystyrene) and evaporated at a current strength of 12 amp. In another series of experiments the sample was placed at different depths on the bottom of the channel of the carbon electrode, and, after filling the remaining volume of the channel by carbon powder, it was evaporated under the same conditions. The parameters of the oscillating circuit and the value of the interelectrode gap were chosen so that in the absence of appreciable amounts of the impurities in the source plasma, the arc sounded continuously. The impurities were evaporated at two electrode temperatures from the cathode and the anode of a dc arc. During the passage of known and varying amounts of the impurity elements, depending on the element, into the source plasma, the sounding of the arc stops after a certain time. The object of the investigation was to establish the relation between the duration of these pauses and the properties of the evaporating elements and some parameters characterizing the excitation source or the evaporation conditions of the materials on the electrodes. In Fig. 4 are shown curves

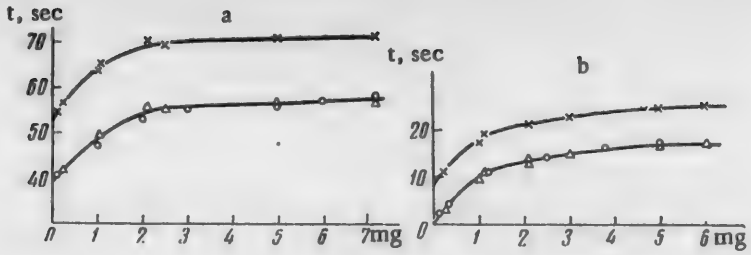


Fig. 7. Relation between the silent time of the arc (t) and the Na content (r = 0.98 A) in Th (r = 0.95 A) and in Be (r = 0.34 A) during their evaporation from carbon electrodes at a depth of 7 mm (a) and 1 mm (b). ×) Na was introduced into Th by coprecipitation; Δ) Na was introduced into Th by mechanical mixing; ●) Na in Be – whichever method is used for introducing the impurity into the base.

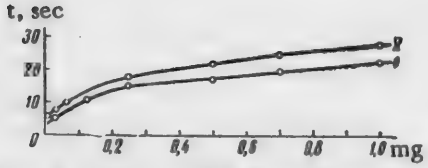


Fig. 8. Curve $t = f(C)$ for sodium in the absence (1) and in the presence (2) of the γ-active isotope of the element ($Na^{24}$) in the sample.

expressing the relation between the duration of a sound pause and the concentration of the various elements during their evaporation from the face of the anode (on the left) or cathode (on the right) treated with polystyrene, of a dc "sounding" arc in the form of the compounds indicated on the Fig. The general appearance of these curves are similar for the various elements. In all cases, at relatively low contents of the elements, there is observed a fairly sharp and almost linear relation between the duration of the pause and the amount of the element evaporating from the electrode. During evaporation of large amounts of an element (greater than 0.2-0.3 mg) the slope of the line which expresses the relation between the duration of a pause and the concentration decreases. The relation between the duration of the silent period of the "sounding" arc and the ionization potential of the atoms of the evaporating elements, their volatility, and the mean temperature of the source plasma are illustrated by the results given in the Table and in Fig. 5.

As one might expect, the time for which the arc ceases to sound during evaporation of the same amount of various elements (1 mg in the case considered) on the electrodes differs. It is strongly dependent on the volatility of the element or of its compounds (see, e.g., the results relating to the readily volatile $ZnCl_2$ or aluminum in the form of the metal or its oxide), while in cases where the volatility is similar, the silent period is determined primarily by the ease with which ionization of the atoms of the elements occurs in the plasma. In the latter case, as experiment shows, the value of $\log t$ is a linear function of the ratio $E/T$. During evaporation of a sample from the cathode, the silent period of the "sounding" arc increases regularly in accordance with the change in the evaporation rate of the elements, which we determined by means of labelled atoms, from the depth of the electrode crater (Fig. 6).

Under conditions such that formation of a melt is excluded, the value of $t$ also depends on the nature of the entry of the impurities into the crystal lattice of the base material (Fig. 7). In those cases where isomorphous penetration of the impurity atoms into the crystal lattice of the base is possible (Na in Th, Fig. 7), there is observed a difference in the duration of the sound pause (t) during evaporation from the crater of a carbon electrode of the same amount of impurity introduced into the base chemically or by mechanical mixing. For ratios of the ionic radii of the impurity atoms to those of the base material (Na in Be, Fig. 7) which are unfavorable from the point of view of isomorphism, the relationship indicated between the character of the evaporation of the impurity and the method whereby it is introduced into the base material is not observed. Thus, in experiments with a "sounding" arc it is again possible to confirm the conclusion reached as to the effect of the trapping of the impurities by the crystal lattice of the base, on the nature and rate of their evaporation, conclusions which some of us arrived at earlier [3, 4] by means of labelled atoms.

Examination of the curves shown in Fig. 8 leads to curious conclusions on the effect of γ -radiation on the operation conditions of a "sounding" arc. They illustrate the relation between the length of the silent period of the "sounding" arc and the amount of sodium evaporating on the anode surface in the absence and in the presence of the γ -active isotope $Na^{24}$.

As is evident, the additional irradiation of the plasma volume by γ -rays, which is achieved in the second case thanks to the presence of the radioactive isotopes of the element, increases the sensitivity of the "sounding" arc to the sodium passing into its interelectrode gap, and permits detection, by means of the "sound" signal, of smaller amounts of the element passing into the plasma of the source. However, how far it will be possible to increase the sensitivity of the determination of elements by means of a "sounding" arc, using the effect detected, and how effective will prove irradiation of the interelectrode gap of the "sounding" arc by ionizing radiation or by an electron beam, can only be shown by further experimental work.

The authors wish to thank V. A. Kosterina for help in the experimental work.

## SUMMARY

It has been shown that the use of a "sounding" arc permits one to follow the passage of materials into the source plasma, and to record the accidental (random) breakdown of the normal course of this process during spectrographic analysis. It can be used for increasing the reproducibility and reliability of the quantitative determination of elements.

It has been shown experimentally that the main parameter which characterizes the operation of a "sounding" arc – the duration of the sound signals and pauses – depends on the concentration of the impurities evaporating on the electrode, their volatility, the ionization potential of the atoms of these elements, the source temperature, and some other factors. In a number of cases the authors have succeeded in establishing the nature of these relationships.

## LITERATURE CITED

[1] A. K. Rusanov, Spectrographic Analysis of Ores and Minerals [in Russian] (Gosgeolizdat, 1948) p. 62.

[2] Yu. I. Belyaev and É. E. Vainshtein, Zhur. Anal. Khim. 14, 133 (1959).*

[3] Yu. I. Belyaev, Thesis, GEOKhI, AN SSSR, Moscow, 1957.

[4] É. E. Vainshtein, L. I. Pavlenko, and Yu. I. Belyaev, The Use of Radioactive Isotopes in Spectrographic Analysis. Reports of the Academy of Sciences, USSR, at the International Conference on the Use of Radioisotopes in Scientific Research, Paris, 1957.

* Original Russian pagination. See C. B. Translation.

# DETERMINATION OF POTASSIUM PRESENT AS AN IMPURITY IN RUBIDIUM CHLORIDE BY A FLAME PHOTOMETRIC METHOD

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There are no reliable and rapid methods for the determination of potassium, rubidium, and cesium in each other's presence, particularly when one of these elements is present in considerable excess. Hitherto, several papers have been published on the flame photometric analysis of mixtures of potassium, rubidium, and cesium [1-3]. Poluéktov and Nikonova [3] used the method of additions for the determination of lithium, sodium, potassium, and rubidium in cesium salts. However, the method of additions is only applicable for very low concentrations of the elements to be determined. For potassium the limits of application are 0.004-0.005% and for rubidium and cesium 0.01-0.008%.

Our work was carried out on a ISP-51 spectrograph provided with a FÉP-1 photoelectric setup. The latter consists of an output collimator connected to a ISP-51 spectrograph with an amplifier and a recording mechanism for recording the spectra of weak radiation (luminescence, combination scattering). When a FÉU-17 photoelectric multiplier is replaced by a FÉU-22 or a VÉI multiplier, then the setup becomes suitable for the analysis of mixtures of the alkaline metals. The prism system of the ISP-51 spectrograph is rotated by means of the electric motor of the FÉP-1 setup, the motor being connected via a cord shaft with the handle of the rotating mechanism of the spectrograph prism. The readings of the rotational angle of the prism are carried out on the drum scale of a setup rotating synchronously with scales similar to that of the reading drum of the spectrograph. The linear dispersion of the setup for $\lambda$ 471.3 m$\mu$ does not exceed 32 A/mm. The rate at which the ribbon of the ÉPP-09 potentiometer moves can be regulated from 60 to 9600 mm/hour. The maximum amplifying factor of the dc amplifier is $10^6$. The setup, in contrast to self-made spectrophotometers based on a UM-2 monochromator, permits determinations to be carried out by the internal standard method.

Spectrophotometers operating on the internal standard method are usually provided with two photomultipliers or photoelements (in the photometers), one of which records the intensity of the impurity line, and the other records that of the internal standard. Shifting the spectrum in front of the output slit of the setup and simultaneously synchronizing the focussing of the various parts of the spectrum on the photomultiplier cathode can be avoided by using one photomultiplier. The atomizer was fed with compressed air from a small compressor fitted with a reservoir. For an air pressure in front of the atomizer of 0.28 kg/cm$^2$, the latter required 0.04 ml/sec of the test solution. The acetylene pressure was kept at a level of 110-160 mm water. The pressure of the air and acetylene was kept constant during a determination. The input slit varied from 0.03 to 0.08 mm and the output slit from 0.05 to 0.1 mm, depending on the experimental conditions. The rate at which the potentiogram was shifted was 360 mm/hour. The dark current was compensated by an appropriate setting of the zero of the setup's power supply potentiometer. In order to avoid lowering the sensitivity of the photoelectric multiplier during its first minutes of operation, the photoelectric setup was switched on for 15-20 minutes beforehand, while at the same time a solution containing approximately the maximum (from the relevant measurement) concentration of the impurity to be determined, was sprayed into the flame.

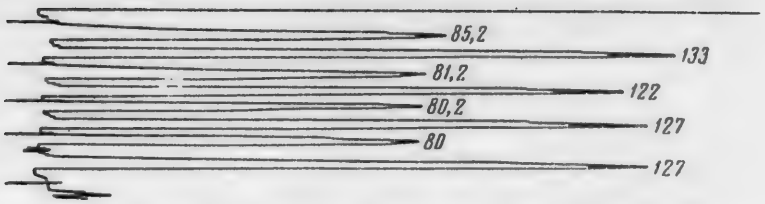


Fig. 1. General appearance of a potentiogram. The small peaks are recordings of the intensity of the spectral line of the impurity, while the large peaks are recordings of the weakened intensity of the spectral line of the internal standard. The figures at the peak tips indicated the values of their ordinates (in mm).

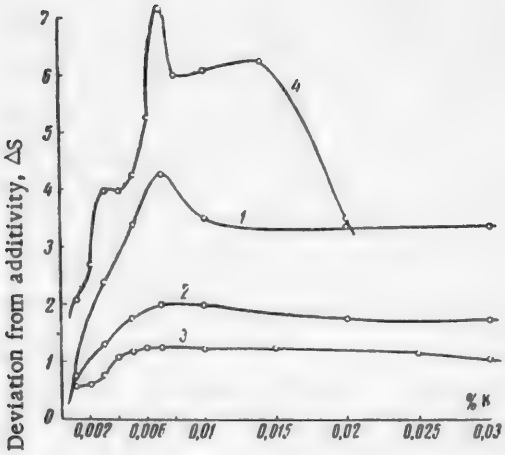


Fig. 2. Δ-Diagram. 1 and 2) Curves illustrating the deviation from additivity for a RbCl concentration of 6 g/100 ml for inlet and outlet slits of 0.1/0.025 mm and 0.07/0.02 mm, respectively; 3 and 4) curves for the deviation from additivity for a RbCl concentration of 4 g/100 ml, using inlet and outlet slits of 0.07/0.02 mm and 0.15/0.03 mm, respectively.

The rubidium chloride used for preparing the standards was purified from potassium by the chlorostannate method. The amount of potassium remaining (0.0001-0.0003%) was determined by the method of additions, and was taken into account when working out the analytical results. Chemically pure-grade potassium chloride was recrystallized twice from water and was checked for freedom from rubidium and cesium.

The standard solutions were prepared by dissolving 2.2 g of rubidium chloride in 50 ml of distilled water (which was checked for absence of potassium). Nine ml lots of this solution were transferred by means of a calibrated pipet into small beakers; to each of these beakers was then added 1 ml of potassium chloride solution of varying concentrations. Each beaker (standard) thereby contained 4 g RbCl/100 ml. The standards were successively measured photometrically by means of the resonance lines – 766.5 mμ for potassium and 780 mμ for rubidium. The relative intensity rather than the absolute intensity of the impurity line was measured, using the main element of the standard as reference element. In order to cut down the intensity of the spectral line of the internal standard (otherwise the pen of the photoelectric setup potentiometer went off the scale) a neutral filter type NS-8, 4 mm thick, was used. For a wavelength of 640 mμ the transmission of the filter was not greater then 7.6%. The filter indicated is included in the kit of the SF-4 spectrophotometer. Other types of neutral filters can also be used. The filter was fitted into a special mounting, which in turn was fitted onto the tube of the inlet slit before exposing the line of the internal standard to the input slit of the photoelectric setup. For each standard, the line of the impurity and the line of the internal standard was measured photometrically in turn not less than three times. The mean arithmetic values of the potentiogram ordinate were taken for calculation. The most suitable lines of the internal standard for potassium would be the rubidium spectral lines 761.9 mμ or 775.8 mμ. Unfortunately, the acetylene-air flame does not cause the appearance of these lines on the potentiogram.

In order to calculate the concentration it is desired to determine, we used a calibration curve which relates the logarithm of the relative intensity ($\log I_{standard}/I_{internal\ standard}$) to the logarithm of the concentration ($\log C_{standard}$), where $I_{standard}$ is the average reading of the spectrophotometer for the standard, $I_{internal\ standard}$ is the reading for the internal standard, and $C_{standard}$ is the concentration of the standard.

TABLE 1

Results Used for Constructing the Calibration Curve

| Standards | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | Sample A |
|---|---|---|---|---|---|---|---|---|---|
| Potassium content of the standard, % | | 0,0021 | 0,0031 | 0,0051 | 0,0071 | 0,01 | 0,015 | 0,020 | 0,0054 |
| Mean value of $I_K/I_{Rb}$ | Line 1 | 0,309 | 0,345 | 0,516 | 0,726 | 1,110 | 1,442 | 1,807 | 0,609 |
| | Line 2 | 0,357 | 0,364 | 0,597 | 0,816 | 1,103 | — | — | 0,650 |

TABLE 2

Results of Analyses by the One-Standard Method

| Potassium content, % | | Mean value of $I_K/I_{Rb}$ | | Potassium found in the sample, % | Error, % (relative) |
|---|---|---|---|---|---|
| standard | sample | standard | sample | | |
| 0,007 | 0,0054 | 0,692 | 0,586 | 0,006 | 11,1 |
| 0,007 | 0,0054 | 0,728 | 0,487 | 0,0046 | 14,8 |
| 0,007 | 0,0054 | 0,764 | 0,590 | 0,0054 | 0,0 |
| 0,005 | 0,0054 | 0,640 | 0,700 | 0,0056 | 3,7 |
| 0,005 | 0,0054 | 0,579 | 0,590 | 0,0052 | 3,7 |
| | | | | Mean error, % (relative) | 6,6 |

TABLE 3

Effect of Various Impurities on the Determination of Potassium in Rubidium Chloride

| Impurity introduced | Potassium content of the sample, % | Concentration of the impurity in the sample, % | | | | |
|---|---|---|---|---|---|---|
| | | 0,001 | 0,01 | 0,05 | 0,1 | 0,5 |
| | | potassium found in the sample, % | | | | |
| Na | 0,005 | 0,004 | 0,005 | 0,005 | 0,005 | 0,005 |
| | 0,008 | 0,008 | 0,008 | 0,008 | 0,007 | 0,007 |
| Cs | 0,005 | 0,005 | 0,005 | 0,005 | 0,005 | 0,005 |
| | 0,008 | 0,008 | 0,008 | 0,008 | 0,008 | 0,008 |
| Ca | 0,005 | 0,005 | 0,005 | 0,005 | 0,005 | 0,006 |
| | 0,01 | 0,009 | 0,01 | 0,01 | 0,009 | 0,009 |
| Mg | 0,005 | 0,005 | 0,005 | 0,005 | 0,005 | 0,005 |
| | 0,01 | 0,009 | 0,008 | 0,009 | 0,008 | 0,008 |

Note: The experimental results were rounded off to the first significant figure.

By measuring the intensity of the impurity line ($I_{impurity}$) with respect to the weakened intensity of the internal standard ($I_{internal\ standard}$), from log $I_{impurity}/I_{internal\ standard}$), it is possible to find on the curve

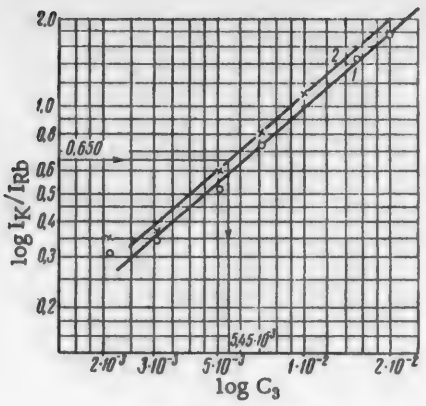


Fig. 3. Calibrations lines.

$\log C_{impurity}$, i.e., the concentration it is required to determine. By using a logarithmic scale it is possible to simplify all the calculations. The general appearance of one of the potentiograms is shown in Fig. 1.

It was observed that with increasing concentration of the main material in the sample, the growth of the emission of the test element reaches a definite limit, beyond which there is no further change in the emission. Changes in the emission of the impurity is observed at a concentration of the main element which does not exceed 1 g/100 ml. Similar observations, but only on cesium salts, were made by Poluektov and Nikonova [3]; the intensity of the potassium (0.0005-0.05%) radiation and rubidium (0.001%) radiation did not change, starting from a 0.5% solution of cesium chloride.

The effect of the main alkali metal of the sample on the radiation intensity of the other alkali metal present as an impurity, and which it is desired to determine, is particularly clearly seen on constructing a Δ-diagram. Should potassium chloride only be present in the test solution, then the spectrophotometer would give a reading $E_K$, while a solution of rubidium chloride only would give a spectrophotometer reading of $E'_{Rb}$ (when the spectrophotometer is adjusted for the spectral line of potassium). When potassium and rubidium chloride are present together one would expect the spectrophotometer pen to give a reading of $E_K + E'_{Rb}$ mm. In actual fact one always gets a reading $S_K > E_K + E'_{Rb}$. The difference $\Delta S = S_K - (E_K + E'_{Rb})$ demonstrates a deviation from additivity (Fig. 2). It should be observed that the background of the flame on its own (that is when the atomizer is not in operation) in the spectral region considered is vanishingly small [4]. The background caused by the main element of the sample was taken into account in the value $E'_{Rb}$. The deviation from additivity for the intensity of the components of the test solution is caused, as is well-known, by a number of factors which we shall not consider here (by the ionization and displacement of the ionization equilibrium, widening of the spectral lines, determined by the concurrent action of collison and the Doppler effect, etc.).

It follows from Fig. 2 that the region in which this deviation from additivity is observed (the region of the greatest mutual influence) lies at concentrations of 0.005-0.01% potassium. Accordingly, in order to develop a method of determining potassium in rubidium chloride, the original concentrations of potassium present as an impurity were chosen as 0.005-0.01%, for a concentration of the main element in the sample of 4 g/100 ml. This enabled us to avoid the use of too-large inlet and outlet slits. Higher concentrations of the main element led to difficulties in the operation of the atomizer.

In Fig. 3 are shown two calibration lines 1 and 2, constructed on a logarithmic scale from the results of Table 1. These two calibration lines correspond to different settings of the spectrophotometer (slits, air and acetylene pressure). Using these two lines 1 and 2, the same synthetic mixture (sample A) containing 0.0054% potassium was analyzed several times. The mean square arithmetical error was ± 0.0002, while the experimental error was −3.7% (relative).

Bearing in mind the comparative complexity of preparing rubidium chloride standards with low potassium contents, we checked on the possibility of using one standard in the flame photometric method. For this purpose the potentiograms of the standard and of the sample were recorded, the mean value of $I_K/I_{Rb}$ was calculated for the standard, and a point marked out on the calibration curve on the basis of the value obtained. Through the point thus obtained was drawn a new calibration curve parallel to the previous calibration curve.

Results of the analysis of sample A by this technique are given in Table 2. Each standard (sample) was measured photometrically at least three times. The mean arithmetic values of the potentiogram ordinate were taken for calculation. The mean square arithmetic error of the potentiogram ordinate did not exceed ± 5.5 mm, while the deviation of the results of individual measurements from their arithmetic mean did not exceed the mean error of a separate measurement by more than twice. The mean square arithmetic error of the analytical results obtained on using the one-standard method amounted to ± 0.00041 for a concentration of 0.0054% of the impurity to be determined. Our observations showed that in most cases, large errors are connected with the operation of the atomizer and the way in which it is fed, but are completely independent of the potentiometer.

A study was also made of the effect on the experimental accuracy of sodium, cesium, calcium, and magnesium chlorides, which are usually present as impurities in technical rubidium chloride.

It is clear from Table 3 that for the indicated amounts of potassium in rubidium chloride, the impurities listed above (with the exception of magnesium) have almost no effect on the accuracy of the determination when they are present in the sample in amounts up to 0.5%. Higher concentrations of these impurities in the sample affect the normal operation of the atomizer as a result of the increase in the viscosity of the solution being sprayed. Magnesium in amounts greater than 0.1% causes a decrease in the emission of potassium, when the concentration of the latter is 0.01%; this confirms published results.

Determination of rubidium in potassium chloride does not differ in any way from the determination of potassium in rubidium chloride.

## SUMMARY

A flame photometric method has been developed for the determination of potassium present as an impurity in rubidium chloride, by means of an ISP-51 spectrograph coupled with a FÉP-1 photoelectric setup. The method recommended permits the development of a general scheme for the determination of certain alkali metals present as impurities in the water-soluble salts of other alkali metals.

## LITERATURE CITED

[1] H. Freitag, Z. anal. Chem. 136, 161 (1952).

[2] Sch. Fukushima, M. Shigemoto, I. Kato, and K. Otozai, Mikrochim. acta 1, 35; 2, 183 (1957).

[3] N. S. Poluéktov and M. P. Nikonova, Zavodskaya Lab. 24, 528 (1958).

[4] N. S. Poluéktov, Analytical Methods by Flame Photometry [in Russian] (Goskhimizdat, Moscow, 1959) p. 101.

# GRAVIMETRIC DETERMINATION OF SMALL AMOUNTS OF BERYLLIUM IN ORES AND IN PRODUCTS OBTAINED DURING THEIR TREATMENT

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For the analysis of materials with a high beryllium content either the gravimetric complexono-phosphate method [1], or the iodometric titrimetric method [2] are usually used. The photometric beryllon method is used for the determination of microgram amounts [3]. These methods, however, do not always ensure sufficiently high accuracy for the analysis of ore materials with beryllium contents ranging from 0.1 to 2-3%. A number of methods have been suggested for the determination of such amounts of beryllium in pure solutions; they include: the method of Benedetti-Pichler [4], in which beryllium sulfate is used as the gravimetric form; the method of Dutta and Sen Gupta [5] which consists of precipitating and weighing $BaBeF_4$, and also other methods of precipitating beryllium in the form of a complex compound with quinaldine [6], and in the form of $[Co(NH_3)_6]\cdot[(H_2O)_2Be_2(CO_3)_2(OH)_3]\cdot 3H_2O$ [7]. There is no published information on the use of these methods for the determination of beryllium in ores.

In a previous communication [8] it was shown that 2,2-dimethylhexanedione-3,5 can be used for the quantitative determination of beryllium in solutions of its pure salts. This reagent forms a sparingly soluble complex compound with beryllium.

The present article is devoted to a description of a method for the determination of beryllium by means of the diketone indicated, in ores and in their processed products.

2,2-Dimethylhexanedione-3,5 was synthesized as described previously [9]. An aqueous solution of the diketone saturated with the latter at room temperature was used as the precipitant, the solution was prepared 2-3 days prior to use in order to give time for a keto-enol equilibrium to be established. Since the diketone indicated is not a sufficiently selective reagent for beryllium, sodium ethylenediaminetetracetate (EDTA-Na) was used as a masking agent.

Even a considerable excess of EDTA-Na has no effect on the completeness of precipitation of beryllium from aqueous solutions (Table 1).

A solution of ammonia can be used instead of pyridine for establishing the requisite pH in the presence of EDTA-Na. In this case the optimum pH range for precipitation is 7-8, while the amount of the saturated solution of the reagent required for precipitating 1 mg of beryllium is 15-20 ml.

Table 2 contains results for the determination of beryllium in the presence of the elements which accompany it most often; they include: aluminum, iron, calcium, and also the rare earths, $UO_2^{2+}$ and $Ti^{4+}$.

As is evident, none of the elements indicated interfere with the determination of beryllium. Tin, which under the conditions used for precipitating beryllium does not form such stable compounds with EDTA-Na, interferes. Tin, however, only rarely accompanies beryllium. In most beryllium ores the elements which interfere with its determination by the suggested method, are absent. Phosphate ions do not interfere even at a

TABLE 1

Determination of Beryllium in the Presence of EDTA-Na (2.04 mg Be taken)

| Molar ratio [Be]:[EDTA-Na] | Be found, mg | Molar ratio [Be]:[EDTA-Na] | Be found, mg |
|---|---|---|---|
| 1:1 | 2,02 | 1·8 | 2,02 |
| 1:2 | 2,04 | 1:10 | 2,03 |
| 1:4 | 2,04 | 1:20 | 2,03 |
| 1:6 | 2,05 | 1:30 | 2,03 |

TABLE 2

Determination of Beryllium in the Presence of Foreign Elements

| Be taken, mg | Foreign element | Amount of foreign element, mg | Be found, mg | Be taken, mg | Foreign element | Amount of foreign element, mg | Be found, mg |
|---|---|---|---|---|---|---|---|
| 2,11 | $Fe^{3+}$ | 200 | 2,11 | 1,02 | $Ca^{2+}$ | 10 | 1,01 |
| | | 200 | 2,10 | | | 20 | 1,01 |
| 2,11 | $Al^{3+}$ | 600 | 2,11 | | | 30 | 1,02 |
| | | 600 | 2,13 | 1,02 | $Ti^{4+}$ | 10 | 1,02 1,02 |
| 2,04 | $Ce^{3+}$ | 10 | 2,04 | | | 20 | 1,01 1,01 |
| | | 20 | 2,03 | 1,02 | $UO_2^{2+}$ | 10 | 1,02 |
| 2,04 | $Nd^{3+}$ | 10 | 2,04 | | | 20 | 1,01 |
| | | 20 | 2,03 | | | 30 | 1,02 |

TABLE 3

Determination of Beryllium in Ores

| Sample wt., g | Be content found by the suggested method, % | Mean Be content, % | Be found, % by the complexono-phosphate method | Be found, % by the radioactivation method | Sample wt., g | Be content found by the suggested method, % | Mean Be content, % | Be found, % by the complexono-phosphate method | Be found, % by the radioactivation method |
|---|---|---|---|---|---|---|---|---|---|
| 1,0 | 0,0461; 0,0475; 0,0454 | 0,0465 | 0,0483 | 0,050 | 1,0 | 0,0972; 0,0961; 0,0965 | 0,0972 | 0,0846 | 0,972 |
| 0,25 | 0,233; 0,234; 0,232 | 0,233 | — | 0,240 | 1,0 | 0,0727; 0,0720; 0,0720 | 0,0722 | 0,0727 | 0,0802 |
| 0,25 | 0,487; 0,483; 0,476 | 0,482 | — | 0,482 | 0,25 | 0,483; 0,482 | 0,482 | — | 0,500 |
| 0,5 | 0,156; 0,150; 0,150 | 0,152 | — | 0,159 | 0,5 | 0,139; 0,137; 0,136 | 0,136 | — | 0,122 |

molar ratio of Be: $PO_4$ of 1: 100; fluoride ions only start to interfere at a molar ratio of Be: F = 1: 20, while carbonate ions start interfering at 1: 30. $SO_4^{2-}$, $Cl^-$, $NO_3^-$, $CH_3COO^-$ do not interfere with the determination.

Determination of beryllium in ores reduces to the following. 0.25-1.0 g of material (depending on the expected beryllium content) is fused in a platinum basin with five times its amount of potassium bifluoride in a muffle furnace at 800-900°. The melt is treated with 15 ml of $H_2SO_4$ 1: 1, and the solution is evaporated until fumes of sulfuric acid cease to be evolved.

The contents of the basin are transferred to a 400 ml beaker, 10 ml of HCl 1: 1 is added, and the volume of the solution made up to 100 ml, and then boiled until the salts have dissolved completely. Where

necessary, the solution is filtered through a "white band" filter paper and cooled to room temperature.* 35-40 ml of a 5% solution of EDTA-Na is then added, and the pH of the solution adjusted to 7-8 with ammonia (using universal indicator); having withdrawn the glass rod from the beaker, diketone solution at the rate of 20-30 ml for each mg of beryllium expected to be present is added to the beaker. The solution is mixed by adding 15-20 ml of water to it.

On adding the reagent the solution becomes turbid, and, after 2-3 hours the precipitate collects into coarse, friable flocs on the bottom of the beaker, and the supernatant solution becomes completely clear. Needle-like crystals are visible under the microscope. The precipitate is then filtered through a No. 4 filter crucible, it is washed several times with cold distilled water and is finally dried to constant weight at 45-55°. During the latter stage care must be taken to ensure that the temperature does not exceed 70-75°, when the precipitate starts to volatilize.

Two 40 minute dryings are sufficient to bring the precipitate to constant weight. The conversion factor to beryllium is 0.03096.

The results obtained are given in Table 3.

The suggested method for the determination of beryllium has a number of real advantages over the complexono-phosphate method. The beryllium compound which corresponds strictly to the formula $Be(CH_3-CO-CH=CO-C(CH_3)_3I_2$; can be prepared by carrying out the precipitation operation once; this cuts down the analysis time considerably. Beryllium is precipitated in the form of a crystalline precipitate, which is easy to wash and can be brought to constant weight at low temperatures. The small conversion factor to beryllium is also very favorable.

## SUMMARY

A description is given of a new gravimetric method for the determination of beryllium in ores and in their processed products; beryllium is precipitated in the form of its compound with 2,2-dimethylhexanedione-3,5. Elements which are complexed by EDTA-Na (Fe, Al, $UO_2^{2+}$, Ti, Ce, Nd, and Ca) do not interfere with beryllium determination. $PO_4$ ions and appreciable amounts of F and $CO_3$ do not interfere either. Tin must be removed.

## LITERATURE CITED

[1] V. G. Goryushina, Zavodskaya Lab. 21, 148 (1955).

[2] V. G. Goryushina and G. A. Archakova, Zavodskaya Lab. 22, 532 (1956).

[3] B. S. Tsyvina and N. K. Davidovich, Zavodskaya Lab. 23, 280 (1957).

[4] A. Benedetti-Pichler and T. Schneider, Microchem. Emich. Festschrift 1 (1930).

[5] R. K. Dutta and A. K. Sen Gupta, J. Indian Chem. Soc. 33, 146 (1956).

[6] K. Motejima, Bull. Chem. Soc. Japan 29, 29 (1956).

[7] T. J. Pirtea and G. Mihail, Z. analyt. Chem. 159, 205 (1958).

[8] E. S. Przheval'skii and L. M. Moiseeva, Zhur. Anal. Khim. 15, 117 (1960).**

[9] D. S. Breslow and C. K. Hauser, J. Am. Chem. Soc. 62, 2385 (1940).

* When the sample contains tin, the latter is removed by precipitating it with hydrogen sulfide in an acid medium.

** Original Russian pagination. See C. B. Translation.

# SEPARATION OF STRONTIUM AND CALCIUM BY MEANS OF SODIUM ETHYLENEDIAMINETETRACETATE (EDTA-Na) DETERMINATION OF STRONTIUM IN APATITES

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In a previous paper [1] the possibility was demonstrated of separating strontium and calcium by precipitating strontium as its sulfate from complexon-containing solutions. On the basis of these results we have carried out a more detailed study of the conditions for precipitating strontium and calcium sulfates from solutions containing sodium ethylenediaminetetracetate (EDTA-Na) and developed a technique for the quantitative separation of these elements at various ratios of one element to the other. The work carried out showed that precipitation of strontium sulfate in the presence of EDTA-Na starts at a pH of about 6, and proceeds quantitatively at pH's lower than 5. Precipitation of calcium sulfate starts at pH's below 4. Separation of strontium and calcium can be achieved at pH 4-5. From solutions of strontium and calcium salts containing sufficient EDTA-Na to complex both elements, strontium is completely precipitated by ammonium sulfate at a pH of about 4.5, while calcium remains in solution.

The necessary condition for the complete separation of strontium is the presence of sufficiently large amounts of ammonium sulfate and moderate amounts of EDTA-Na in solution.

When the relative amounts of strontium are considerable, separation of strontium from calcium proceeds quite satisfactorily in an aqueous medium. When the calcium predominates, then the EDTA-Na content of the solution becomes too high for precipitation of the strontium, as a result of which some of the latter may remain in solution with calcium. In such cases, completeness of separation of strontium can be ensured by addition of ethanol.

Depending on the content and proportions of strontium and calcium, the following two variants are suggested for separating and determining strontium and calcium in their mixtures.

Separation of large amounts of strontium from calcium. The method described below is applicable to mixtures containing strontium and calcium in the proportion of 1:5 and higher.

The mixture of strontium and calcium oxides is dissolved in the minimum amount of dilute nitric (or hydrochloric) acid. To the solution containing not more than 150 mg of oxides is added EDTA-Na at the rate of 800 mg per 100 mg of the oxides, after which a few drops of methyl red is added as indicator and ammonia added until the solution is yellow in color. Ten ml of a 10% solution of ammonium sulfate is added and the total volume of the solution made up to 30-45 ml. To the heated solution is added dropwise dilute sulfuric acid to the appearance of a stable rose color (pH about 4.5) and the solution plus precipitate left for 20-30 min at 70-80°. After two hours the precipitate is filtered through a small dense filter and is washed 5-6 times with water containing a small amount of ammonium sulfate. Strontium is finally determined gravimetrically or titrimetrically. In the first case the precipitate is calcined at a dark-red heat and weighed as $SrSO_4$. For the titrimetric variant, the precipitate plus filter are transferred back again into the beaker and is dissolved in the cold in an ammoniacal solution of EDTA-Na. Excess of the EDTA-Na is titrated with magnesium chloride using

TABLE 1

Separation of Strontium from Calcium in Aqueous Solution

| Taken, mg | | Sr found, mg | Error in the determination of Sr | |
|---|---|---|---|---|
| Sr | Ca | | mg | % |
| 20,4 | 10 1 | 20,6 | +0,2 | ,0 |
| 20,4 | 20,2 | 20,1 | —0,3 | 5 |
| 20,4 | 105,8 | 20,3 | —0,1 | 0,5 |
| 10,2 | 100 | 9,4 | —0,8 | 8 |
| 5,4 | 100 | 4,1 | —1,3 | 24 |

acid chrome-blue or eriochrome black T—tropeoline 00 as indicator. The calcium content of the mixture is calculated by difference, or is determined gravimetrically after precipitation of calcium in the filtrate in the form of its oxalate [4].

Results for the determination of strontium and calcium by this variant are given in Table 1. Strontium was determined titrimetrically. As is evident from the results adduced, the relative error for the determination of strontium at ratios of Sr: Ca ranging from 2: 1 to 1: 5 is about 1%. At lower strontium ratios the error increases appreciably; in such cases it is accordingly necessary to use the second variant of the method.

Separation of small amounts of strontium from large amounts of calcium. This variant is applicable for strontium contents not less than 1 mg and not more than 200 mg calcium.

The calcium and strontium oxides are dissolved in the minimum amount of nitric (or hydrochloric) acid. To the solution containing not more than 100 mg of the oxides is added EDTA-Na at the rate of 800 mg per 100 mg of the oxides, after which a few drops of methyl red is added followed by ammonia until the solution is yellow in color. The volume of the solution is made up to 30 ml and dilute sulfuric acid added until a rose color is obtained. Ten ml of an acetate buffer with a pH of 4.5 is then added (250 ml of 98% acetic acid and 100 ml of concentrated ammonia per liter) this is followed by 10 ml of a 10% solution of ammonium sulfate and 10 ml of 96% ethanol. When strontium is present, a milky turbidity of strontium sulfate appears after 1-2 minutes, or immediately (depending on the amount of strontium). After 24 hours the precipitate which has separated out is filtered through a double "blue band" filter paper, it is washed 5-6 times with 50% alcohol containing a small amount of ammonium sulfate, and is finally calcined to a dark-red heat and weighed as $SrSO_4$.

When the amount of the oxides in solution exceeds 100 mg good results can be obtained by carrying out a reprecipitation, since in such cases there is a possibility that calcium may be partially precipitated. For this purpose, the sulfate residue, after weighing, is returned to the beaker and EDTA-Na added (5-10 mg per mg of residue), ammonia is added until its odor is clearly distinguishable. The solution is heated until the precipitate has dissolved, after which it is acidified with dilute sulfuric acid using methyl red as indicator, 5 ml of the acetate buffer and 5 ml of ammonium sulfate solution are finally added. The total volume of the solution is made up to 25 ml and an equal volume of alcohol added. After 24 hours the precipitate which has separated out is filtered off, and washed 5-6 times with 50% alcohol containing a small amount of ammonium sulfate; it is finally calcined at a dark-red heat and weighed as $SrSO_4$.

The calcium content of the mixture can be calculated by difference, or can be determined directly after precipitation of calcium from the filtrate in the form of its oxalate.

This variant was checked on synthetic mixtures for ratios of Sr: Ca ranging from 1: 100 to 2: 1, in which the absolute amounts of strontium varied from 20 to 1 mg. The experimental results obtained (Table 2) showed that even under the most unfavorable ratios of strontium and calcium (Sr: Ca from 1: 100 to 1: 20), the relative error for the determination of strontium does not exceed 10%. At higher strontium contents this error is usually about 1%.

The purity of the separated precipitates was checked spectrographically. It was found that on separating mixtures containing strontium and calcium in the proportion 1: 10, contamination of strontium sulfate by calcium is about 1%. Strontium was found in traces in the CaO residue.

Determination of strontium in apatites. Precipitation of $SrSO_4$ from solutions containing the complexon permits the possibility of a simple and rapid determination of strontium in apatites. In this case there is no need for a preliminary separation of total strontium and calcium. Direct precipitation of strontium sulfate in the presence of EDTA-Na enables it to be separated not only from calcium, but also from all the other elements present in apatite.

TABLE 2

Separation of Strontium from Calcium in an Aqueous-Alcoholic Medium

| Taken, mg | | Sr found, mg | Error in the determination of Sr | | Ca found (gravimetrically), mg |
|---|---|---|---|---|---|
| Ca | Sr | | mg | % | |
| 1000 | 0.9 | 0.9 | 0 | 0 | – |
| 100 | 1.8 | 1.9 | +0.1 | +5.5 | – |
| 100 | 2.7 | 2.8 | +0.1 | +3.7 | – |
| 100 | 3.6 | 3.9 | +0.3 | +8.3 | – |
| 100 | 4.8 | 4.8 | 0 | 0 | – |
| 100 | 10.0 | 10.0 | 0 | 0 | – |
| 51.2 | 10.0 | 10.1 | +0.1 | +1.0 | 50.8 |
| 51.2 | 20.0 | 20.2 | +0.2 | +1.0 | 50.8 |
| 10.2 | 10.0 | 10.0 | 0 | 0 | 10.4 |
| 10.2 | 20.0 | 20.1 | +0.1 | +0.5 | 10.5 |

TABLE 3

Results of the Determination of Strontium in Apatites

| Sample No. | Strontium content, % | |
|---|---|---|
| | by the chemical method | by a mass-spectrographic method |
| 430a | 8,27 | 8,26 |
| 203a | 4,07 | 4,11 |
| 849a | 2,28 | 2,20 |
| 338 | 4,72 | 4,71 |
| 220 | 2,28 | 2,25 |

0.2 g of apatite is dissolved in nitric acid and 10 ml of a 10% solution of EDTA-Na added, a few drops of methyl red is then added, followed by ammonia until the solution is yellow. The solution is carefully acidified until a rose color appears, when 10 ml of the acetate buffer with pH 4.5, and 10 ml of 10% ammonium sulfate solution are added. The total volume is made up to 50 ml, after which an equal volume of 96% ethanol is added. After 24 hours the precipitate which has separated out is filtered off, washed 5-6 times with 50% alcohol containing a small amount of ammonium sulfate; it is finally calcined at a dark-red heat and weighed as $SrSO_4$.

This method was checked by determining strontium in five samples of apatites. In order to control the results obtained, in parallel with its chemical determination, the strontium content of the mineral was also determined mass-spectrographically by the isotope dilution technique.

The determination was carried out as follows. 0.02 g of sample was dissolved in a few drops of nitric acid after which a known amount of indicator solution with the following isotopic composition was added: $Sr^{84}$ – 57.1%, $Sr^{86}$ – 7.6%, $Sr^{87}$ – 3.9% and $Sr^{88}$ – 31.4%. The solution was carefully mixed, and, after addition of EDTA-Na, the strontium was precipitated with ammonium sulfate at a pH of 4.5, and alcohol added. The isolated strontium was placed on the ribbon of the ionic source directly, in the form of its sulfate after dissolving it in concentrated sulfuric acid. The isotopic composition was determined on a MI-1305 mass-spectrometer by a technique adopted in the Dokembrya Geological Laboratory, Academy of Sciences, USSR [3]. The ratio $Sr^{84}/Sr^{88}$ was measured. The strontium content of the sample taken was calculated by means of the formula:

$$X = \frac{Sr^{84}_{cm}(1{,}85 - K)}{K} \cdot 0{,}682,$$

where X is the strontium content of the sample; $Sr^{84}$ cm is the $Sr^{84}$ content of the aliquot of indicator taken; 1.85 is the $Sr^{84}/Sr^{88}$ ratio in the indicator; and K is the ratio $Sr^{84}/Sr^{88}$ in the mixture obtained.

Results of the chemical and mass-spectrographic determinations of strontium are compared in Table 3. The good agreement obtained shows that the value obtained by the chemical method gives the true strontium content of the sample, and is not the result of a compensation of errors.

## SUMMARY

A method has been developed for the quantitative separation of strontium and calcium; it is based on precipitation of strontium as its sulfate in the presence of EDTA-Na at a pH of 4.5. The method has been checked on synthetic mixtures of strontium and calcium in which the ratios of the two elements Sr: Ca varied from 2: 1 to 1: 100, and in which the absolute amount of strontium varied from 1 to 20 mg.

A simple and rapid method has been developed for the determination of strontium in apatites, and it has been compared with a mass-spectrographic isotope dilution method.

## LITERATURE CITED

[1] L. I. Afanas'eva, Zhur. Anal. Khim. 14, 294 (1959).*

[2] R. Pribil, Complexons in Chemical Analysis [Russian translation from Czech) (IL, Moscow-Leningrad, 1955).

[3] E. K. Gerling, M. L. Yashchenko, L. K. Levskii, and G. V. Ovchinnikova, Geokhimiya, No. 6, 535 (1958).

* Original Russian pagination. See C. B. Translation.

# COMPLEXONOMETRIC DETERMINATION OF ALUMINUM WITH AN AMPEROMETRIC INDICATION OF THE TITRATION END POINT

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Direct complexonometric determination is possible for $Mg^{2+}$, $Ca^{2+}$, $Sr^{2+}$, $Ba^{2+}$, $Zn^{2+}$, $Hg^{2+}$, $Cd^{2+}$, $Pb^{2+}$, $Al^{3+}$, $Bi^{3+}$, $Ni^{2+}$, $Co^{III}$, $Fe^{3+}$, $Mn^{2+}$, some of the rare earths, Zr, and Th [1-5]. In addition, by back titration, or by some other indirect complexonometric method, it is also possible to determine a number of other metals (Al, Ga, Zr, Ag, Au, Pd, Pt, and Na). Several papers have been devoted to the complexonometric determination of aluminum, but only in one of them is there suggested a direct determination of aluminum [6] in an acid solution using pyrocatecholsulfonphthalein as an indicator; in the remaining papers various back-titration methods were used [7-11].

Complexonometric indicators have quite clearly expressed drawbacks. This, to a certain degree, limits the application of sodium ethylenediaminetetracetate (EDTA-Na), particularly during the determination of aluminum in various objects.

Physicochemical methods of indicating the end point (potentiometry, amperometry) without doubt considerably expand the possibilities of the use of EDTA-Na. However, as far as aluminum is concerned, these methods are not used sufficiently. The only method known is a determination of aluminum by a back-potentiometric titration [4]. Several methods have been published on the amperometric determination of aluminum using sodium fluoride and 8-hydroxyquinoline [12-14]. We have been unable, however, to find in the literature any references to the amperometric titration of aluminum using EDTA-Na.

Aluminum can be determined amperometrically by direct titration with EDTA-Na, which, as Usatenko and Vitkina [15, 16] have shown, gives an anodic diffusion wave on a rotating platinum microanode. It is more expedient to carry out a back titration of excess EDTA-Na with a ferric salt, which, as is known, also gives a diffusion current on a platinum microelectrode. As a first step in the development of a method for the amperometric titration of aluminum by means of EDTA-Na, we chose a back-titration technique.

## EXPERIMENTAL

Amperometric titration was carried out on an ordinary setup with a rotating platinum electrode as an indicator, without applying an external emf. The reference electrode was a saturated calomel electrode connected to the titration vessel via an agar-agar bridge.

The electrode was rotated at a rate of 700 rpm. The type M 198/1 galvanometer used had a sensitivity of $1 \cdot 10^{-8}$ per scale division.

* Deceased.

TABLE 1

Determination of Aluminum (0.400 mg Al taken)

| Al found, mg | Error | |
|---|---|---|
| | mg | % |
| 0.406 | 0.006 | 1.5 |
| 0.409 | 0.009 | 2.25 |
| 0.400 | – | – |
| 0.403 | 0.003 | 0.75 |

Titration was carried out in 50 ml vessels.

The EDTA-Na solution was prepared by dissolving an aliquot and then standardizing the solution against $MgSO_4$.

The concentration of the ferric chloride solution was determined iodometrically.

Initially, conditions for determination of $Al^{3+}$ in solutions of its pure salts were established. Experiments were carried out as follows. To 1 ml (titer – 0.004 g) of a standard solution of an aluminum salt, prepared by dissolving an accurately weighed aliquot of aluminum metal, was added 5 m of 0.1 M EDTA-Na solution; this was followed by 0.2 ml $CH_3COONH_4$ (50% solution) in order to adjust the pH to 5. The pH was controlled by universal indicator paper. The volume of the solution was made up to 25 ml with distilled water and was finally titrated with 0.1 M ferric chloride solution.

The results obtained (Table 1) show that aluminum can be determined fairly accurately in pure solutions, by amperometric titration with EDTA-Na.

There are published references to the fact that magnesium cations form a stable complex in an alkaline medium [4].

The logarithms of the instability constants [17] of magnesium, aluminum, and iron have the following values:

| | | |
|---|---|---|
| for magnesium | ethylenediaminetetracetate | 8.69; |
| for aluminum | " | 16.13; |
| for iron | " | 25.1 |

Only the most stable complexes are formed in acid solutions, this gives the possibility of titrating with a ferric salt not only the free acid EDTA, but also EDTA-Mg. We have checked on the possibility of determining aluminum in the presence of magnesium. During the determination of $Al^{3+}$ in the presence of various amounts of $Mg^{2+}$ at ratios of Al:Mg = 1:10, 1:12.5, completely accurate results were obtained in 16 experiments, the relative error was 0% even for the highest magnesium contents, while in four experiments it did not exceed 2.5%.

The presence of large amounts of magnesium does not interfere with aluminum determination. We have also established that the presence of small amounts of zinc does not affect the accuracy of aluminum determination.

For the determination of aluminum in alloys based on magnesium (88.8% Mg, 0.05% Fe) by the proposed method, an aliquot of 1 g is dissolved in 20 ml HCl (1:1), the solution is transferred to a 200 ml standard flask and its volume made up to the mark with distilled water. One ml of this solution is transferred to a 50 ml beaker, 2 ml of 0.1 M EDTA-Na and 0.2 ml of $CH_3COONH_4$ (50% solution) are added, and the volume made up to 25 ml with distilled water; the solution is finally titrated with 0.1 M ferric chloride.

The end point is found graphically. The aluminum content is calculated by means of the formula:

$$\frac{[v_1-(v_2a)]\,TP\cdot b\cdot 100}{v_k}\%\ \text{Al},$$

where $v_1$ is the volume of EDTA-Na in ml; $v_2$ is the volume of ferric chloride in ml; $\underline{a}$ is the amount of EDTA-Na in ml corresponding to 1 ml of ferric chloride solution; T is the titer of EDTA-Na with respect to aluminum in g; P is the weight of alloy in mg; $\underline{b}$ is the amount in ml of the solution of the alloy taken for titration; and $v_k$ is the volume of the flask in ml.

Results for the determination of aluminum in several samples of magnesium alloys by the method suggested, and by the GOST 3240-56 gravimetric method "Magnesium Alloys," are given in Table 2.

Other impurities in the alloys analyzed (0.25% Zn, and 0.05% each of Cu, Mn, Ni, and Fe) are contained in such small amounts that they show almost no effect on the determination of aluminum.

TABLE 2

Determination of Aluminum in Alloys

| Alloy | Aluminum found | | deviation, % |
|---|---|---|---|
| | by a gravimetric method | by the amperometric method | |
| MA-331 | 7.67 | 7.88 | 0.21 |
| MA-331 | 7.67 | 7.67 | – |
| | 7.67 | 7.77 | 0.10 |
| MA-422 | 9.11 | 9.18 | 0.07 |
| | 9.11 | 9.32 | 0.21 |
| | 9.11 | 9.32 | 0.21 |
| MA-904 | 7.91 | 8.10 | 0.19 |
| | 7.91 | 7.91 | – |
| | 7.91 | 8.01 | 0.10 |

TABLE 3

Tempometric Titration of Mixtures of Aluminum and Magnesium

| Series | Expt. No. | Experiment time, sec | Mean time, sec | Aluminum taken | | Amount of magnesium | |
|---|---|---|---|---|---|---|---|
| | | | | mg | ml | mg | ml |
| I | 1 | 192,2 | 192,7 | 2 | 0,5 | 35,52 | 1 |
| | 2 | 192,6 | | | | | |
| | 3 | 192,8 | | | | | |
| | 4 | 193,2 | | | | | |
| II | 1 | 159,2 | 158,9 | 4 | 1 | 35,52 | 1 |
| | 2 | 159,2 | | | | | |
| | 3 | 158,4 | | | | | |
| | 4 | 158,8 | | | | | |
| | 5 | 159,0 | | | | | |
| III | 1 | 125 | 125,2 | 6 | 1,5 | 35,52 | 1 |
| | 2 | 125,6 | | | | | |
| | 3 | 125,2 | | | | | |
| | 4 | 125 | | | | | |
| IV | 1 | 94,2 | 95,2 | 8 | 2 | 35,52 | 1 |
| | 2 | 95,4 | | | | | |
| | 3 | 95,8 | | | | | |
| | 4 | 94,8 | | | | | |
| | 5 | 96,0 | | | | | |
| V | 1 | 61,0 | 60,6 | 10 | 2,5 | 35,52 | 1 |
| | 2 | 60,6 | | | | | |
| | 3 | 61,0 | | | | | |
| | 4 | 59,8 | | | | | |

An attempt was made to increase the accuracy and cut down the analysis time by the method proposed and by the GOST 3240-56 method "Magnesium Alloys" set forth and described in a number of papers [18, 19]. In the drop-tempometric method, the concentration of the test material is determined by means of a calibration curve, on whose abscissa time is plotted, while on the ordinate concentrations of standard solutions are plotted.

In Fig. 1 is shown a schematic diagram of a setup for the amperometric titration of aluminum by a drop-tempometric method without application of an external emf. The accuracy of tempometric titration depends to a considerable extent on the uniform supply of solution from the buret. For this purpose a tempometric buret (m) was adopted, this buret, which has a constant difference in the liquid levels (h), ensures an uniform supply of solution. The discharge rate was controlled by means of a capillary (k) and was equal to 10 drops in 11 sec.

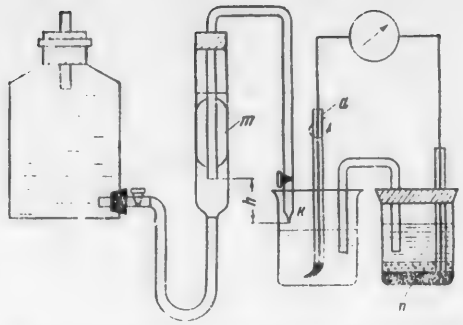


Fig. 1. m) Tempometric buret; k) capillary; a) rotating platinum electrode; n) saturated calomel electrode.

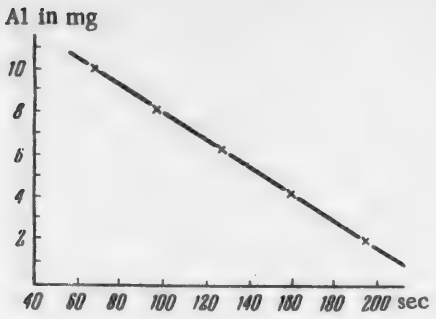


Fig. 2.

TABLE 4

Determination of Aluminum in Alloys

| Alloy | Found, % | | Deviation, % | Duration of titration, sec |
|---|---|---|---|---|
| | by a gravimetric method | by the tempometric method | | |
| MA-422 | 9,11 | 9,14 | +0,03 | 149,9 |
| | 9,11 | 9,11 | — | 150,4 |
| | 9,11 | 9,01 | —0,10 | 151,0 |
| | 9,11 | 9,07 | —0,04 | 150,8 |
| | 9,11 | 9,13 | +0,02 | 150,0 |
| MA-331 | 7,67 | 7,65 | —0,02 | 161,8 |
| | 7,67 | 7,71 | +0,04 | 161,4 |
| | 7,67 | 7,67 | — | 162,0 |
| | 7,67 | 7,72 | +0,05 | 161,2 |
| | 7,67 | 7,59 | —0,08 | 162,6 |
| MA-904 | 7,91 | 7,80 | —0,011 | 161,0 |
| | 7,91 | 7,90 | —0,001 | 160,6 |
| | 7,91 | 7,80 | —0,11 | 161,0 |
| | 7,91 | 7,86 | —0,05 | 160,8 |

The order in which the tempometric method was carried out was as follows: the beaker containing the test solution was placed in the apparatus and the rotating platinum electrode switched on. At the same time the tap of the tempometric buret was opened and a stopwatch started. Titration was regarded as complete when the galvanometer needle started to shift rapidly from its original position. At this point the stopwatch was switched off and the tap of the tempometric buret turned off. The concentration of the test solution was determined from a calibration curve of "time against concentration of standard solution."

The standard solution was prepared so that the same amount of magnesium (35, 52 mg) was contained in the volume to be titrated, while the amount of aluminum was changed (2, 4, 6, 8, 10 mg). The results obtained are given in Table 3.

A calibration curve was constructed from the results obtained by the titration of a standard mixture (Fig. 2). The aluminum content of magnesium alloys was determined by means of this curve (Table 4).

The sample was dissolved and prepared for analysis by the same method as that used for the amperometric titration.

The second variant of determining aluminum in magnesium alloys gives the most accurate results, while an analysis is carried out in half the time taken for the first variant. The analysis time is cut down by using

the semiautomatic method of supplying the solution, and by determining the end point during continuous titration visually, by following the galvanometer needle. In the titration of two parallel samples in which the volume was measured the time taken was 30-35 min, while by the tempometric method the time taken was 3.5 min.

Taking into account that the method of preparing the alloy for analysis is the same in both variants, the saving in time obtained is determined solely by the improved method of titration.

The time taken to determine aluminum in magnesium alloys, including decomposition of the sample, is 30 min. Thus, the drop-tempometric method of determining aluminum by the proposed method is an express method.

## SUMMARY

An amperometric method is suggested for the determination of aluminum in magnesium alloys by means of EDTA-Na, without removing the aluminum from the other components. The experimental accuracy is about 0.2% (absolute).

On the basis of the method suggested a rapid and accurate tempometric method of determining aluminum in magnesium alloys has been developed.

## LITERATURE CITED

[1] V. G. Goryushina, Zavodskaya Lab. 20, 447 (1954).

[2] K. B. Yatsimirskii, Zavodskaya Lab. 21, 1449 (1955).

[3] K. B. Yatsimirskii, Zavodskaya Lab. 21, 1275 (1955).

[4] R. Pribil, Complexons in Chemical Analysis [Russian translation from Czech] (IL, Moscow, 1955).

[5] A. I. Busev and N. G. Polyanskii, The Use of Organic Reagents in Inorganic Analysis [in Russian] (Izd. AN SSSR, Moscow, 1958) p. 47.

[6] M. Malat, V. Suk, and O. Ryba, Chem. Listy 48, 208 (1954); Ref. Zhur. Khim. 32884 (1954).

[7] H. Flaschka and H. Abdiena, Mikrochim. Acta N 1, 37 (1955); Ref. Zhur. Khim. 52149 (1955).

[8] K. A. Hegedus, Sapok 9, N 7, 333 (1954); Ref. Zhur. Khim. 11861 (1955).

[9] G. W. C. Milner and S. L. Woodhead, Analyst 79, 363 (1954).

[10] K. ter Haar and J. Bazen, Anal. Chim. Acta 10, 23 (1954).

[11] E. Wanninen and A. Ringbom, Anal. Chim. Acta 12, 308 (1955).

[12] Yu. I. Usatenko and G. E. Beklesheva, Zavodskaya Lab. 19, 147 (1953).

[13] Yu. I. Usatenko and G. E. Beklesheva, Zavodskaya Lab. 20, 266 (1954).

[14] A. K. Zhdanov and N. K. Kozhevnikov, Zavodskaya Lab. 18, 529 (1952).

[15] Yu. I. Usatenko and M. A. Vitkina, Nauch. Dokl. Vysshei Shkoly. Khim. i Khimicheskaya Tekhnologiya, No. 3, 502 (1958).

[16] Yu. I. Usatenko and M. A. Vitkina, Zavodskaya Lab. 24, 1058 (1958).

[17] K. B. Yatsimirskii and V. P. Vasil'ev, Instability Constants of Complex Compounds [in Russian] (Izd. AN SSSR, Moscow, 1959) p. 173.

[18] A. K. Kal'e, Trudy Komis. po Anal. Khim. Akad. Nauk SSSR 1 (IV), 1947, p. 190.

[19] A. K. Kal'e, Zavodskaya Lab. 13, 413 (1947).

# RESEARCH IN THE ANALYTICAL CHEMISTRY OF THALLIUM

## COMMUNICATION 5. A STUDY OF COMPLEXONOMETRIC INDICATORS FOR TRIVALENT THALLIUM*

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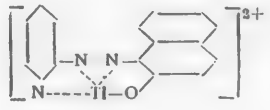
Comparatively few color reactions are known for trivalent thallium ions. Chromotropic azo dyes, for example, give a color effect with thallium [1]. There are almost no indicators for the complexonometric determination of thallium at low pH values when the selectivity of the method is comparatively high. Of interest, accordingly, was a study of the interaction of trivalent thallium at pH 2 with a complexonometric indicator recently suggested [2], namely 1-(2-pyridylazo)-2-naphthol, and also with 1-(2-pyridylazo)-resorcinol, and xylenol orange (the latter has been used by Kinnunen and Wennerstrand [3] for titrating thallium at pH 4-5).

The aim of our work was to determine the equilibrium constant and the optical characteristics of the reagents employed, and of the compounds formed by them with trivalent thallium, in order to choose the optimum conditions for their use as complexonometric indicators.

1. The interaction of trivalent thallium with 1-(2-pyridylazo)-2-naphthol. A $5.816 \cdot 10^{-4}$ M solution of the reagent in methanol was used in the work; it was prepared by dissolving an accurately weighed amount of the preparation synthesized by Chichibabin's method [4]; its m. p. was 138°.

1-(2-Pyridylazo)-2-naphthol forms with trivalent thallium a red-violet-colored compound which is rather sparingly soluble in water; its solubility increases in the presence of organic solvents which are miscible with water such as methanol, ethanol, and acetone. The best solvents of those which are immiscible with water are the higher alcohols and carbon tetrachloride.

The light-absorption curves taken on a SF-4 spectrophotometer with an incandescent lamp show that at pH 4.5 solutions of 1-(2-pyridylazo)-2-naphthol have a maximum light absorption at 470 mμ; this maximum, on addition of a trivalent thallium salt, shifts to 560 mμ (Fig. 1). Using the method of isomolar series (for a total molar concentration of $1.163 \cdot 10^{-4}$ M, and pH of 2.2) it was established that thallium and 1-(2-pyridylazo)-2-naphthol react in a molar ratio of 1:1 (Fig. 2). Taking into account that in dilute solutions multinuclear complexes are not formed, it can be assumed that formation of a complex cation occurs:



* For communication 4 see Zhur. Anal. Khim. 15, 291 (1960) [See C. B. translation].

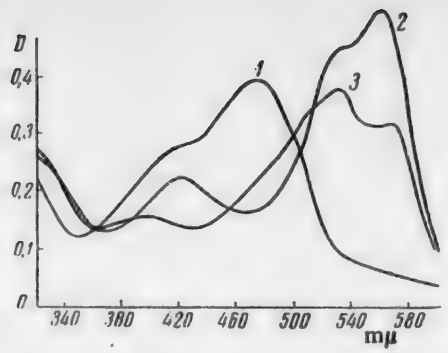



Fig. 1. Light-absorption curves of a $2.33 \cdot 10^{-5}$ M solution of 1-(2-pyridylazo)-2-naphthol: 1) at a pH of 4.5; 2) in the presence of tenfold molar excess of $Tl^{3+}$ salt at pH 4.5; 3) in 0.1 M NaOH; $l = 1$ cm.

TABLE 1

Relation between Cl/D and the Compound of Thallium with 1-(2-Pyridylazo)-2-naphthol

| C, M | D | Cl/D | $1/\sqrt{D}$ |
|---|---|---|---|
| $5,82 \cdot 10^{-5}$ | 1,92 | $6,1 \cdot 10^{-5}$ | 0,72 |
| $4,65 \cdot 10^{-5}$ | 1,40 | $6,6 \cdot 10^{-5}$ | 0,84 |
| $3,49 \cdot 10^{-5}$ | 0,92 | $7,6 \cdot 10^{-5}$ | 0,04 |
| $2,91 \cdot 10^{-5}$ | 0,71 | $8,2 \cdot 10^{-5}$ | 1,19 |
| $2,33 \cdot 10^{-5}$ | 0,475 | $9,8 \cdot 10^{-5}$ | 1,45 |
| $1,74 \cdot 10^{-5}$ | 0,280 | $12,4 \cdot 10^{-5}$ | 1,89 |
| $1,16 \cdot 10^{-5}$ | 0,175 | $13,3 \cdot 10^{-5}$ | 2,39 |

In order to determine the equilibrium constant of the complex formation reaction of trivalent thallium with 1-(2-pyridylazo)-2-naphthol, and the molar light absorption coefficient of the compound thereby formed, the method of Komar' as modified by Tolmachev [5] was used; Tolmachev's modification consists of interpreting the results graphically. The experimental method reduces to measuring the light absorption at 560 mμ of a series of colored solutions of varying concentration, in which the ratio of the concentration of the metal ion to the concentration of the addendum was kept constant and equal to 1:1 in accordance with the molar ratio established. All the solutions contained 50% (by volume) of methanol in order to increase the solubility of the thallium compound; the hydrogen ion concentration was kept constant by means of a buffer solution with a pH of 2.2 prepared from 0.1 M $KHC_8H_5O_6$ and 0.1 M $HClO_4$. The temperature of the test solutions was 20 ± 1°. The layer thickness of the cuvette was $l = 1.997$ cm. The results obtained are given in Table 1.

The straight line within the coordinates $Cl/D - (1/\sqrt{D})$ has a slope of $5.48 \cdot 10^{-5}$ and cuts a segment $4.6 \cdot 10^{-5}$ on the ordinate, which is numerically equal to the reciprocal of the true molar coefficient of light absorption. From this:

$$\varepsilon = \frac{1}{4,6 \cdot 10^{-5}} = 2,17 \cdot 10^{4}.$$

The equilibrium constant will be:

$$K = \frac{10^{-2,2} \cdot 1,997}{2,17 \cdot 10^{4} (5,48 \cdot 10^{-5})^{2}} = 1,93 \cdot 10^{2}.$$

Knowing the values of the equilibrium constant, it is possible to determine the stability of the complex as a function of the pH. 1-(2-Pyridylazo)-2-naphthol is a very weak acid; cleavage of the proton from the hydroxy group, which is accompanied by a color change from yellow to red-violet, starts at pH > 11. The concentration of free $R^-$ ions depends essentially on the pH, in the same way that the stability of the complex with thallium also depends on the pH. $K'_{stab} = K_{stab} / a_H$ where $a_H = 1 + [H^+]/K_{HR}$:

$$K_{stab} = \frac{[TlR^{2+}]}{[Tl^{3+}][R^-]} = \frac{[TlR^{2+}][H^+]}{[Tl^{3+}][HR] \cdot K_{HR}} = \frac{equil}{K_{HR}};$$

$$K'_{stab} = \frac{K_{equil}}{K_{HR}\left(1 + \frac{[H^+]}{K_{HR}}\right)}; \quad K'_{stab} = \frac{K_{equil}}{K_{HR} + [H^+]}.$$

When $[H^+] >> K_{HR}$, then the value of $K_{HR}$ in the numerator can be ignored. We then get

$$K'_{stab} = \frac{K_{equil}}{[H^+]}.$$

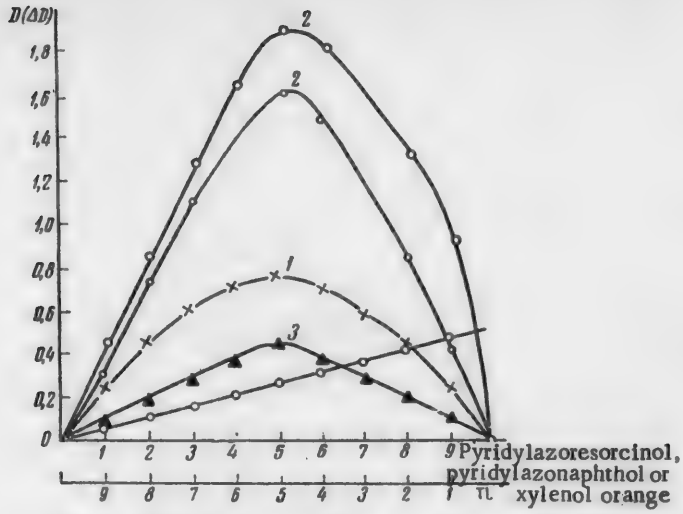



Fig. 2. Curve of "composition against optical density" for the systems: 1) $Tl^{3+}$ – 1-(2-pyridylazo)-2-naphthol; 2) $Tl^{3+}$ – 1-(2-pyridylazo)-resorcinol; 3) $Tl^{3+}$ – xylenol orange.

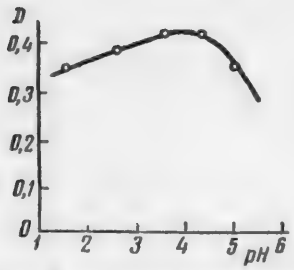



Fig. 3. Relation between pH and the optical density of a solution of the compound of thallium with 1-(2-pyridylazo)-2-naphthol.

The compound formed is not particularly stable at low pH values. The color of the complex increases with increasing pH, and decreases in the region where the trivalent thallium ion hydrolyzes (Fig. 3). Chloride and bromide ions affect the color of the complex strongly, and, in the presence of the latter at pH 1-2, the complex of thallium with 1-(2-pyridylazo)-2-naphthol changes over completely into bromide complexes as soon as a 2-3-fold molar excess of bromide ions is added. Photometric determination of thallium by means of 1-(2-pyridylazo)-2-naphthol is not of practical significance on account of its low selectivity at pH 4-5, and because of the limited solubility of the compound formed.

2. Interaction of trivalent thallium with 1-(2-pyridylazo)-2-resorcinol. A $5.816 \cdot 10^{-4}$ M solution of 1-(2-pyridylazo)-resorcinol was used in this work; this was prepared by dissolving an accurately weighed amount of the base synthesized by Chichibabin's method [6] and having a m. p. of 185-186° in water, and alkalizing the solution.

1-(2-Pyridylazo)-resorcinol reacts with trivalent thallium to form a red-colored compound which is fairly soluble in water, butanol, and isoamyl alcohol, but is insoluble in diethyl ether, benzene, carbon tetrachloride, and chloroform. The reagent is a dibasic acid. The first proton splits off in an acid medium, and the second one in a strongly alkaline medium (starting at pH 11). Actually, the light-absorption curves of a solution of the reagent at pH 1.5 and 5.0-5.5 differ from each other; this is obviously connected with the presence of undissociated molecules ($H_2R$) in equilibrium with $HR^-$ ions at pH 1.5. In the pH range 3-11 almost only $HR^-$ ions with a maximum light absorption at 415 mμ exist. At pH 13 the second proton starts to split off with formation of $R^{2-}$ ions (maximum light absorption 495 mμ). At pH 2.2, the reagent, in the presence of a tenfold molar excess of trivalent thallium salt, has a maximum light absorption at 520 mμ (Fig. 4). The curve "composition – optical density," and also the curve "composition – difference in optical density of the solution and the optical density of the colored reagent," at a constant total molar concentration of the reactants have a maximum at a molar ratio of the components of 1:1 (Fig. 2).

Determination of the equilibrium constant of the reaction of complex formation between trivalent thallium and 1-(2-pyridylazo)-resorcinol, and of the molar light-absorption coefficient of the compound formed

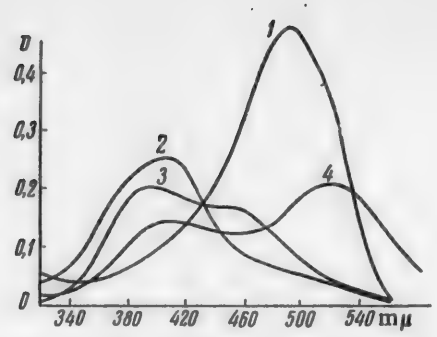



Fig. 4. Light-absorption curves for a $5.81 \cdot 10^{-6}$ M solution of 1-(2-pyridylazo)-resorcinol: 1) in 0.1 M NaOH; 2) at pH 5.5; 3) at pH 1.5; 4) at pH 2.2 in the presence of a tenfold molar excess of $Tl^{3+}$ salt; $l$ = 1.997 cm.

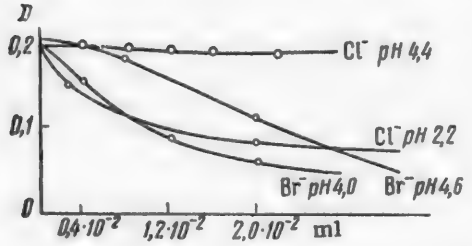



Fig. 5. Relation between the optical density of a $1.16 \cdot 10^{-5}$ M solution of the compound of $Tl^{3+}$ with 1-(2-pyridylazo)-resorcinol and the concentration of halogen ions.

TABLE 2

Determination of the True Molar Extinction Coefficient of the Compound Formed Between Trivalent Thallium and 1-(2-Pyridylazo)-resorcinol

| C, M | D | Cl/D | $1/\sqrt{D}$ |
|---|---|---|---|
| $3,49 \cdot 10^{-5}$ | 1,20 | $5,81 \cdot 10^{-5}$ | 0,91 |
| $2,33 \cdot 10^{-5}$ | 0,78 | $5,96 \cdot 10^{-5}$ | 1,13 |
| $1,74 \cdot 10^{-5}$ | 0,57 | $6,07 \cdot 10^{-5}$ | 1,32 |
| $1,40 \cdot 10^{-5}$ | 0,46 | $6,12 \cdot 10^{-5}$ | 1,47 |
| $1,16 \cdot 10^{-5}$ | 0,37 | $6,29 \cdot 10^{-5}$ | 1,64 |
| $9,31 \cdot 10^{-6}$ | 0,29 | $6,41 \cdot 10^{-5}$ | 1,86 |
| $6,98 \cdot 10^{-6}$ | 0,21 | $6,64 \cdot 10^{-5}$ | 2,18 |

(Table 2) was carried out by the method indicated above at a temperature of 15 ± 1°. The straight line has a slope of $6.40 \cdot 10^{-6}$ and cuts out a segment on the ordinate equal to $5.54 \cdot 10^{-5}$. Accordingly,

$$\varepsilon = \frac{1}{5,54 \cdot 10^{-5}} = 1,805 \cdot 10^4,$$

$$K = \frac{10^{-2,2} 1,997}{1,805 \cdot 10^4 (6,40 \cdot 10^{-6})^2} = 1,70 \cdot 10^4.$$

Using the results obtained (Table 2), we calculated the molar light-absorption coefficient and the equilibrium constant by means of Komar's formulas [7], the assumption being made that at a given wavelength it is not only the colored compound that absorbs but also the reagent itself. The molar extinction coefficient of the acid form of the reagent is $4.3 \cdot 10^3$. The molar coefficient of the compound formed was calculated by means of the formula:

$$\varepsilon_x = \frac{1}{l}\left(\frac{D_i}{C_i} + B\frac{D_i - n D_k}{C_i (n - B)}\right),$$

where $n = C_i/C_k$ (it was chosen so that $2 \leq n \leq 5$),

$$B = \left(\frac{D_i - \varepsilon l C_i}{D_k - \varepsilon l C_k}\right)^{1/2}, \quad \varepsilon = 4,3 \cdot 10^3.$$

The following values of $\varepsilon_x$ were thereby obtained: $1.93 \cdot 10^4$; $1.95 \cdot 10^4$; $1.85 \cdot 10^4$; $1.91 \cdot 10^4$; $2.07 \cdot 10^4$, a mean value of $1.94 \cdot 10^4$. The value of the constant was calculated by means of the formula:

$$\frac{D_i - \varepsilon l C_i}{l(\varepsilon_x - \varepsilon)} = \frac{1}{h} K \left(\frac{C_i l \varepsilon_x - D_i}{l(\varepsilon_x - \varepsilon)}\right)^2$$

where h is the hydrogen ion concentration. The following values of K were obtained: $0.76 \cdot 10^4$; $0.77 \cdot 10^4$; $0.80 \cdot 10^4$; $0.63 \cdot 10^4$; $1.01 \cdot 10^4$; $0.81 \cdot 10^4$; $0.79 \cdot 10^4$, a mean value of $0.80 \cdot 10^4$, i.e., almost half the value obtained graphically without taking into account absorption by the reagent itself at 520 mμ.

In accordance with the greater stability of the complex of trivalent thallium with 1-(2-pyridylazo)-resorcinol, the effect of chloride and bromide ions on its color is not so markedly expressed, particularly at high pH values (Fig. 5). The relation between the color and the pH is similar to that for the compound of thallium with 1-(2-pyridylazo)-2-naphthol (see Fig. 3).

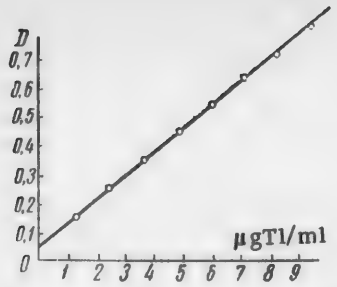



Fig. 6. Calibration curve for photometric determination of thallium by means of 1-(2-pyridylazo)-resorcinol at 520 mμ.

TABLE 3

Relation Between Cl/D and $DY_2$ for the Compound of Thallium with Xylenol Orange

| C, M | D | $\frac{Cl}{D}$ | $\frac{1}{\sqrt{D}}$ |
|---|---|---|---|
| $13,3 \cdot 10^{-6}$ | 0,445 | $5,98 \cdot 10^{-5}$ | 1,50 |
| $11,0 \cdot 10^{-6}$ | 0,348 | $6,31 \cdot 10^{-5}$ | 1,69 |
| $8,9 \cdot 10^{-6}$ | 0,277 | $6,40 \cdot 10^{-5}$ | 1,90 |
| $6,7 \cdot 10^{-6}$ | 0,206 | $6,46 \cdot 10^{-5}$ | 2,20 |
| $4,4 \cdot 10^{-6}$ | 0,127 | $6,98 \cdot 10^{-5}$ | 2,80 |
| $2,2 \cdot 10^{-6}$ | 0,055 | $8,06 \cdot 10^{-5}$ | 4,26 |

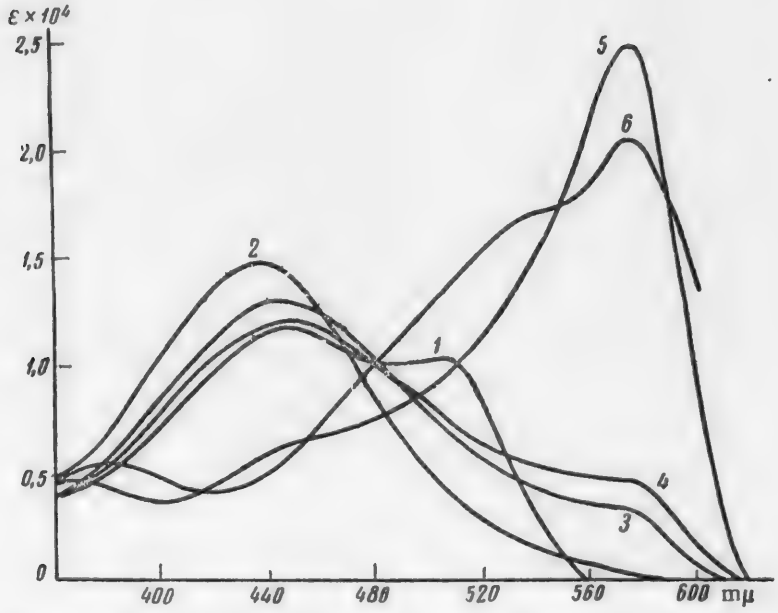
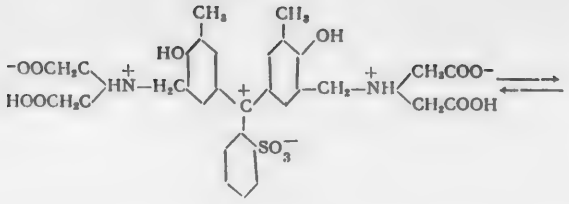



Fig. 7. Light-absorption curves of xylenol orange at various pH values: 1) in 1 M $HClO_4$; 2) at a pH of 3.6; 3) at a pH of 5.4; 4) at a pH of 6.0; 5) at a pH of 8.2; 6) in the presence of a tenfold molar excess of $Tl^{3+}$ salt at pH 5.0.

Colored solutions containing the compound formed between trivalent thallium and 1-(2-pyridylazo)-resorcinol conform to Beer's law over the concentration range 1-10 μg Tl/ml (the optical density was measured at 520 mμ in a cuvette with a layer thickness of 1 cm, the blank solution was water) (Fig. 6).

3. Interaction of trivalent thallium with xylenol orange. Xylenol orange supplied by the "Khemapol" firm was used in the work. The indicator is a sexibasic acid ($H_6R$). In strongly acid solutions it has a rose color and is present in solution in the form of $H_6R$ (I); at pH > 2 the rose color changes to yellow, which is obviously connected with the formation of $H_3R^{3-}$ ions (II). This is accompanied by the splitting off of a proton from one of the OH-groups located in the para position with respect to the central carbon atom (in this pH range, presumably, splitting of protons from two carboxyl groups occurs). At pH > 6 a red-violet color appears which is determined by the change of the indicator into the $H_2R^{4-}$ (III) alkali form. The hydrogen ions in the imino groups possess very weakly expressed acid properties and only split off in a strongly alkaline medium (pH about 11).



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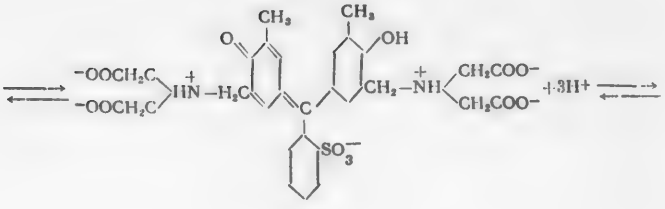
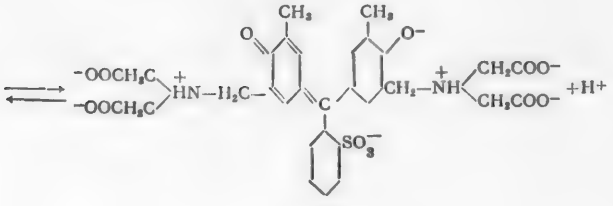


(II)



(III)

The existence in solution, depending on the pH, of three forms is proved by spectrophotometric measurements (Fig. 7).

We have determined the dissociation constant of the second hydroxyl ion of xylenol orange; for this purpose the optical density of $2.0 \cdot 10^{-5}$ M solution of xylenol orange was measured at various pH values up to the point at which the optical value became constant (Fig. 8). Measurements were carried out at 580 mμ. The requisite pH value was achieved by means of buffer solutions prepared by mixing 1/15 M solutions of $Na_2HPO_4$ and $NaH_2PO_4$. The dissociation constant was calculated by means of the formula $K = [H^+]D/[\epsilon([H_6R]_{total}] - D/\epsilon)$, where $\epsilon$ is the molar light extinction coefficient of the alkaline form of the indicator (III) and is equal to 28,000. The dissociation constants were calculated:

| pH | 7,25 | 7,45 | 7,70 | 7,90 | 8,08 | 8,50 |
|---|---|---|---|---|---|---|
| $K$ | $2,6 \cdot 10^{-8}$ | $2,74 \cdot 10^{-8}$ | $1,93 \cdot 10^{-8}$ | $2,15 \cdot 10^{-8}$ | $3,24 \cdot 10^{-8}$ | $2,32 \cdot 11^{-8}$ |

The mean value of $pK_{diss} = 7.6$. From the pH value at which $D = 1/2D_M$, the value $pK_{diss} = 7.7$ (Fig. 8) was determined graphically.

The light-absorption curve of the compound of trivalent thallium with xylenol orange has a maximum at 580 mμ. Using the isomolar-series method for a total molar concentration of $4.44 \cdot 10^{-5}$ M and a constant pH of 2.5, it was shown that trivalent thallium and xylenol orange react in the molar ratio of 1:1 (Fig. 2).

Determination of the equilibrium constant was carried out at pH 1.4 in a series of solutions with varying metal concentrations (Table 3).

The straight line within the coordinates $C1/D - 1/\sqrt{D}$ has a slope of $7.34 \cdot 10^{-6}$ and intersects the ordinate to give a segment equal to $5.0 \cdot 10^{-5}$. Accordingly, $\epsilon = 2.00 \cdot 10^{-4}$, while $K = (10^{1.4} \cdot 5.0 \cdot 10^{-5} \cdot 1.997)/(7.34 \cdot 10^{-6})^2 = 7.39 \cdot 10^4$. In parallel, measurements of the optical density of another series of solutions in a cuvette with a layer thickness of 1 cm gave the following results:

$$\epsilon = 1,96 \cdot 10^4 \text{ and } K = \frac{10^{-1,4} \cdot 5,1 \cdot 10^{-5}}{(5,04 \cdot 10^{-6})^2} = 8,00 \cdot 10^4.$$

the mean value $K_{mean} = 7.7 \cdot 10^4$, and $\epsilon = 1.98 \cdot 10^4$. It is easy to see that the compound of thallium with xylenol orange is the most stable one; this can be explained by the presence in the molecule, apart from OH groups, of two groups of iminoacetic acid which possess a high complexing capacity with respect to multivalent ions.

The investigation which we carried out on the stability of the complexes of thallium with the indicators indicated above, enabled us to determine the minimum permissible pH value at which trivalent thallium can be titrated complexonometrically when these indicators are used.

It is known that [8] an indicator can be used for complexonometric titration as long as the following conditions is obeyed:

$$pC_0 + 2 \leqslant \log K'_{stab} \leqslant \log K''_{stab} - 2,$$

where $C_0$ is the initial concentration of the solution being titrated, $K'_{stab}$ is the "apparent" stability constant of the complexonate at a given pH value, and $K''_{stab}$ is the "apparent" stability constant of the complex of thallium with the indicator at the same pH value.

$$K'_{stab} = \frac{K_{stab}}{a_H}; \quad K_{stab} = 2{,}9 \cdot 10^{23} \text{ [9]}$$

$$a_H = 1 + \frac{[H^+]}{K_4} + \frac{[H^+]^2}{K_3 \cdot K_4} + \frac{[H^+]^3}{K_2 \cdot K_3 \cdot K_4} + \frac{[H^+]^4}{K_1 \cdot K_2 \cdot K_3 \cdot K_4} \qquad (9)^*$$

($K_1$, $K_2$, $K_3$, and $K_4$ are the dissociation constants of ethylenediaminetetracetic acid). Taking into account the dependence of the stability of the complexonate of trivalent thallium and of its complexes with indicators (Fig. 9) on pH, we found that 1-(2-pyridylazo)-2-naphthol can be used as an indicator starting at a pH of 1.8, as long as the initial concentration of the solution of the thallium salt is 0.01 M, while 1-(2-pyridylazo)-resorcinol can be used starting at pH 1.7, and xylenol orange starting at a pH of 2.0.

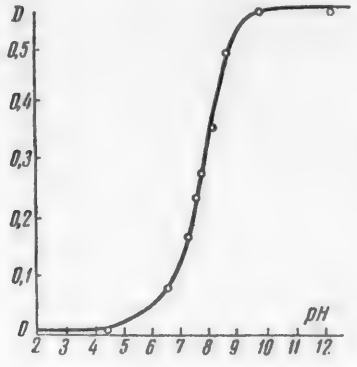



Fig. 8.

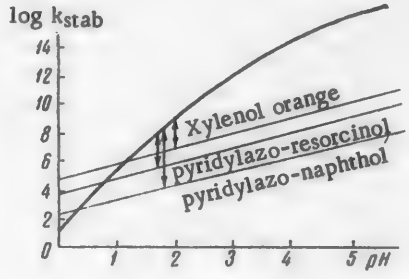



Fig. 9.

Fig. 8. Relation between the optical density of xylenol orange and pH.

Fig. 9. Stability as a function of pH: 1) complexonate of trivalent thallium; 2) the complex of thallium with xylenol orange; 3) the complex of thallium with 1-(2-pyridylazo)-resorcinol; 4) the complex of thallium with 1-(2-pyridylazo)-2-naphthol.

Experimental results are in good agreement with these conclusions. As shown earlier [2], 1-(2-pyridylazo)-2-naphthol can be used as an indicator starting from a pH of 1.8. At the same pH it is possible to use 1-(2-pyridylazo)-resorcinol and xylenol orange, their selectivity, however, is considerably lower than that of 1-(2-pyridylazo)-2-naphthol.

* As in the Russian original.

Calculation of the theoretical errors arising during the complexonometric titration of thallium with the given indicators under the conditions indicated above shows that the titration error is − 0.45% when 1-(2-pyridylazo)-2-naphthol is used as indicator, +0.68% when 1-(2-pyridylazo)-resorcinol is used as indicator, and +1.88% when xylenol orange is used. The calculation reduces to a search for the complexon concentration ($\varphi$) which it is necessary to add to the solution of a trivalent thallium salt at a given pH value, in order that there should be a change in the color of the indicator (or, in other words, in order that the ratio of the concentration of the free indicator to the concentration of the indicator combined by the metal ion be 10:1). The following equilibria occur in the system:

$$Tl^{3+} + H_2O \rightleftarrows TlOH^{2+} + H^+ \qquad pK_1 = 1{,}14$$

$$TlY^- \rightleftarrows Tl^{3+} + Y^{4-*} \qquad pK_2 = 22{,}5$$

$$HTlY \rightleftarrows TlY^- + H^+ \qquad pK_3 = 2{,}3$$

$$Tl^{3+} + HR \rightleftarrows TlR^{2+} + H^+ \qquad K_{equil.} = \frac{[TlR^{2+}][H^+]}{[Tl^{3+}][HR]}.$$

Introducing the designations $[Tl^{3+}] = x$, $[TlOH^{2+}] = y$, $[TlY^-] = z$, $[HTlY] = u$, $[TlR^{2+}] = v$, $[Y^{4-}] = s$, $[HR] = w$, $[H^+] = h$, we obtain:

$$\varphi = z + u + s \cdot a_H \quad (1)$$

$$c = x + y + z + u + v \quad (2)$$ (c is the initial concentration of the solution being titrated)

$$w = 10v \quad (3)$$

$$c_1 = w + v \quad (4)$$ ($c_1$ is the concentration of the indicator added)

$$K_1 x = yh \quad (5)$$

$$K_2 z = xs \quad (6)$$

$$K_3 u = zh \quad (7)$$

$$K_p = \frac{h}{10x} \quad (8).$$

From (1) and (2) we obtain: $c - \varphi = x + y + v - s \cdot a_H$ or $c - \varphi = (h/10K_{equil.}) + [K_1/(10K_{equil.})] + (C_1/11) - [(10K_2 \cdot K_{equil.} \cdot a_H)/h]\,z$; bearing in mind that $\varphi = z + (zh/K_3) + [(10K_2 \cdot K_{equil.} \cdot a_H)/h]\,z$, we have $c - \varphi = \{(h + K_1)/10K_{equil.} + (c_1/11) - (A \cdot B)/[1 + (h/K_3)]\}$, where $A = c - c_1/11 - [(h + K_1)/10K_{equil.}]$, and $B = (10K_2 \cdot K_{equil.} \cdot a_H)/h$.

Assuming that $c = 10^{-2}$, $c_1 = 2 \cdot 10^{-5}$, $h = 10^{-1.8}$, $K_{equilib} = 10^{2.28}$, $a_H = 10^{14.12}$ we get $c - \varphi = 4.5 \cdot 10^{-5}$, from which the titration error is −0.45%. For $h = 10^{-1.7}$ $K_{equilib} = 10^{3.90}$ and $a_H = 10^{14.48}$ we get $c - \varphi = -6.8 \cdot 10^{-5}$, while the error amounts to +0.68%. For $h = 10^{-2.0}$, $K_{equilib} = 10^{4.89}$, $a_H = 10^{13.40}$ we get $c - \varphi = -1.88 \cdot 10^{-4}$, and the titration error is +1.88%.

## SUMMARY

A study has been made of the interaction of trivalent thallium with certain complexonometric indicators: 1-(2-pyridylazo)-2-naphthol, 1-(2-pyridylazo)-resorcinol, and xylenol orange. The composition of the compounds formed by trivalent thallium ions with the reagents indicated has been determined, as well as the equilibrium constants of the complex formation reaction. The molar extinction coefficients of the compounds formed have been calculated. The pH conditions have been established at which the given indicators can be used during the complexonometric titration of trivalent thallium.

## LITERATURE CITED

[1] I. M. Korenman, V. G. Potemkin, and L. S. Fedorova, Zhur. Anal. Khim. 11, 307 (1956).**

[2] A. I. Busev and V. G. Tiptsova, Zhur. Anal. Khim. 13, 180 (1958).**

[3] J. Kinnunen and B. Wennerstrand, Chem. Anal. 46, 34 (1957).

[4] A. E. Chichibabin and M. D. Ryazantsev, Zhur. Russ. Fiz. Khim. Obshchest. 47, 1582 (1915).

[5] V. N. Tolmachev, Trudy Nauch. Issled. Inst. Khim. Khar'kov Universiteta 8, 1951, p. 65.

* The anion of ethylenediaminetetracetic acid.

** Original Russian pagination. See C. B. translation.

[6] A. E. Chichibabin, Zhur. Russ. Fiz. Khim. Obshchest. 50, 516 (1918).

[7] N. P. Komar', Trudy Nauch. Issled. Inst. Khim. Khar'kov Universiteta 8, 1951, p. 51.

[8] K. B. Yatsimirskii, Zavodskaya Lab. 21, 1149 (1955).

[9] A. I. Busev, V. G. Tiptsova, and T. A. Sokolova, Zhur. Neorg. Khim. 5, No. 12, (1960).

# SPECTROPHOTOMETRIC DETERMINATION OF ERBIUM AND HOLMIUM IN SOLUTION

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The absorption spectra of solutions of the salts of most of the rare earths possess a considerable number of narrow, intensive bands in the visible, ultraviolet, and infrared parts of the spectrum. Thanks to the characteristics of the structure of the electronic shells of these elements, their spectra depend to only a small extent on the structure and composition of complexes into which they enter, since the energy levels of the atoms between which transition of $4f$ electrons occur during absorption of light, are protected from the external influence of the filled electronic shell 5S5p. Accordingly, the spectrophotometric determination of the rare earths can be determined in simple solvents: water, alcohols, etc., without resorting to the use of complex organic reagents.

Only a relatively small number of papers have been published on spectrophotometric methods of determining the rare earths, since such methods are considerably less sensitive than the spectrographic method; on the other hand, the spectrophotometric method is more accurate than the spectrographic method. Among recent papers the most interesting are those of Polyakov and Rusanov [1], Wylie [2], and Moeller and Brantley [3]. In [1], which is devoted to the description of a technique for the determination of Pr, Nd, Sm, and Er, a study was made of the effect of other rare earths on the experimental results. In [2] is given a method for the determination of Pr, Nd, and Sm in solution, and a study was made of the effect of the presence of free acid, the ions of other rare earths, and neutral salts. In [3] the absorption spectra of 11 rare earths were measured, these rare earths being in solution in the form of various salts. In developing analytical methods, the effect of the slit width of the spectrophotometer and the presence of foreign anions was taken into account.

We have developed a method for the spectrophotometric determination of Er and Ho in pure aqueous and alcoholic solutions, and in solutions containing dysprosium salts.

The absorption spectra of the chlorides of Er, Ho, and Dy in water and in methanol were carefully measured on a SF-4 spectrophotometer in the region 220-1200 mμ.

By comparing the spectra obtained it was established that the most suitable bands for analytical purposes are 522.2 mμ in aqueous solutions (520.8 mμ in alcoholic solution) for Er, and 536.8 mμ (537.0 mμ in alcoholic solution) for Ho. There are no other intense bands near these, absorption in which could distort the experimental results; the background of the main absorption edge is almost completely absent, so that it is not possible to choose more intense bands in the ultraviolet part of the spectrum. The absorption is high enough — density D = 0.380 and D = 0.267, respectively, for 1% solutions of the chlorides of Er and Ho at a layer thickness of 10 mm. There are no characteristic Dy absorption bands near these bands, so that it is possible to determine Er and Ho spectrophotometrically in Dy solutions.

The absorption bands of Er and Ho chosen for analytical purposes have, however, a complex structure (see Figs. 1 and 2). It was necessary therefore to study the effect of changes in the concentration of the solutions on the ratio of the components of the complex bands in order to eliminate errors which might arise as a result.

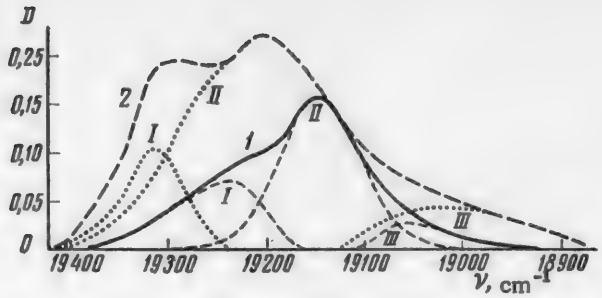


Fig. 1. Absorption band of erbium chloride at 522.2 mμ: 1) aqueous solution; 2) alcoholic solution.

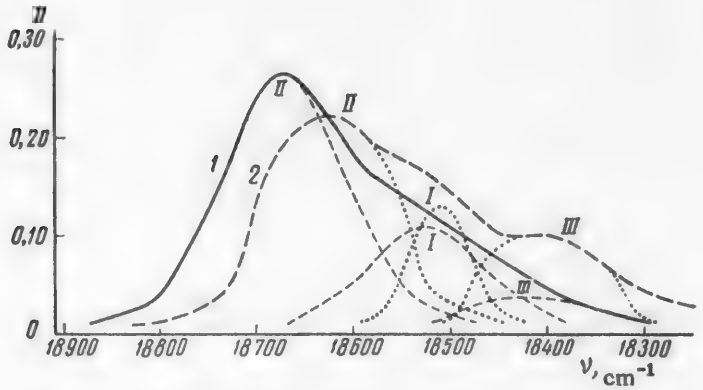


Fig. 2. Absorption band of holmium chloride 536.8 mμ: 1) aqueous solution; 2) alcoholic solution.

Resolution of the complex bands into components was carried out on the basis that their shape should correspond to a Gaussian probability curve. The correctness of this hypothesis is confirmed by the work of Jorgenson [4], in which a detailed examination was made of the shape of the absorption bands in the spectra of salts of elements with incomplete shells, on the basis of a vast amount of experimental data, and in which it was shown that they should have the shape of a Gaussian probability curve. The contour of the complex absorption band of $Er^{3+}$ in aqueous solutions (Fig. 1) has one peak, on the short-wave wing of the contour there is clearly visible a protrusion, while on the long-wave wing there is a very slow drop starting at a density equal to half the maximum density. The contour of the absorption band of $Er^{3+}$ in alcoholic solution is similar to that described, but instead of the protrusion there is a clearly manifested second peak. A study of both contours by the method described previously [5] showed that their long-wave wings are strictly Gaussian for densities $\geq 1/2\, D_{max}$. A preliminary analysis of the sum of the artificially constructed Gaussian curves showed that when the half widths do not differ strongly from each other, then in the case where there is a clearly manifested protrusion or a second peak on the total curve, it is possible to regard the wing of the more intense component as undistorted. Assuming that this rule holds for the experimental curves studied, we completed the contour of the most intense component on the basis of the measured segment of the total curve having a Gaussian form. The remaining two components were obtained by subtracting the constructed Gaussian curve from the measured contour of the band. When this was done it was found that the inner wings of the components obtained by subtraction also have the shape of a Gaussian curve, while the outer wings differ slightly from such a curve, particularly towards the ends, which is possibly caused by the influence of the total absorption background. The following parameters were determined for all the components: the absorption at the maximum $D_0$ and the frequency of the maximum $\nu_0$ (by the numerical differentiation method), the half width of the band $\Delta$ (directly from the contour) and the area S confined by the contour and the frequency axis (by calculation for the Gaussian band, and by measurement with a planimeter for the other two).

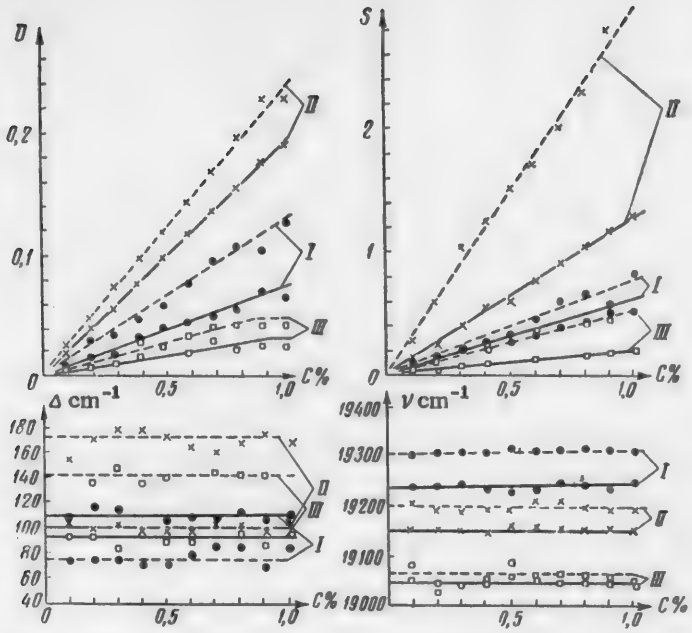


Fig. 3. The relation between the absorption parameters of a complex band and the concentration of the solution: 1) aqueous solution; 2) alcoholic solution.

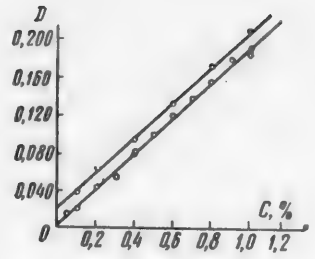


Fig. 4. Beer's law for solutions containing 5% dysprosium. The density values are slightly higher than the density of a pure solution of erbium because of the presence of insignificant amounts of erbium in the dysprosium.

In Fig. 2 their relationship to the concentration of $Er^{3+}$ ions in water and in methanol is shown. The spectra were studied within the concentration range 0.05 to 1.0% Er. The position of all three components in the spectrum, and their half widths are constant, and are independent of the concentration; Beer's law is strictly obeyed and the areas are proportional to the concentration. The half widths in the spectrum of an aqueous solution are similar to each other, while in the spectrum of an alcoholic solution the half width of the first component is twice the half width of the second and third components. The large scatter in the points corresponding to the third component is explained by its low intensity and the difficulty of determining its parameters, which is connected with this. The forces of the oscillators for all the components were calculated by Kravets's method [6].

A comparison of the parameters of the corresponding bands in the spectra of the aqueous and alcoholic solutions shows that all the bands in the spectra of the alcoholic solutions are shifted towards the short-wave side as compared with the spectra of aqueous solutions, the distance between the components in the first case being greater than that in the second case ($\nu_I - \nu_{II} = 90$ cm$^{-1}$ and $\nu_{II} - \nu_{III} = 100$ cm$^{-1}$, respectively). On switching from aqueous to alcoholic solutions, components II and III behave similarly; the half widths of the bands $\Delta$, the absorption coefficients at the maximum $D_0$, and the forces of the oscillators increase: $\Delta_{MeOH}/\Delta_{H_2O} = 1.75$ and 1.49; $D_{MeOH}/D_{H_2O} = 1.32$ and 2.73; $f_{MeOH}/f_{H_2O} = 2.36$ and 2.73, for components II and III, respectively. The change in the parameters of the first component is somewhat different: on switching from aqueous to alcoholic solutions the half width of the band decreases: $\Delta_{MeOH}/\Delta_{H_2O} = 0.68$, while the absorption coefficient and the oscillator force increase: $\Delta_{MeOH}/\Delta_{H_2O} = 1.75$ and $D_{MeOH}/D_{H_2O} = 1.30$. It is known that an increase in the half width of a band is usually related to an increase in the interaction of the absorbing ion with the medium, while the growth of the absorption coefficient and the oscillator force are connected with an increase in the probability of a transition between levels.

TABLE 1

Parameters of the Components of the Complex Absorption Band of $Er^{3+}$ in Aqueous and Alcoholic Solutions

| Band No. | Solvent | $\nu_0$, $cm^{-1}$ | $\Delta$, $cm^{-1}$ | $D$ (in relative units) | $S$ (in relative units) | $f$ |
|---|---|---|---|---|---|---|
| I | $H_2O$ | 19 240 | 110 | 0,37 | 0,41 | $2,3 \cdot 10^{-6}$ |
| | $CH_3OH$ | 19 300 | 75 | 0,65 | 0,55 | $3,0 \cdot 10^{-6}$ |
| II | $H_2O$ | 19 150 | 100 | 1,00 | 1,00 | $0,55 \cdot 10^{-5}$ |
| | $CH_3OH$ | 19 200 | 175 | 1,23 | 2,29 | $1,3 \cdot 10^{-5}$ |
| III | $H_2O$ | 19 050 | 95 | 0,19 | 0,14 | $0,77 \cdot 10^{-6}$ |
| | $CH_3OH$ | 19 060 | 140 | 0,30 | 0,39 | $2,1 \cdot 10^{-6}$ |

TABLE 2

Parameters of the Components of the Complex Absorption Band of $Ho^{3+}$ in Aqueous and Alcoholic Solutions

| Band No. | Solvent | $\nu_0$, $cm^{-1}$ | $\Delta$, $cm^{-1}$ | $D$ (in relative units) | $S$ (in relative units) | $f$ |
|---|---|---|---|---|---|---|
| I | $H_2O$ | 18 670 | 170 | 1,00 | 1,00 | $1,33 \cdot 10^{-5}$ |
| | $CH_3OH$ | 18 620 | 160 | 0,87 | 0,79 | $0,96 \cdot 10^{-5}$ |
| II | $H_2O$ | 18 540 | 175 | 0,41 | 0,45 | $5,45 \cdot 10^{-6}$ |
| | $CH_3OH$ | 18 545 | 90 | 0,48 | 0,25 | $3,02 \cdot 10^{-6}$ |
| III | $H_2O$ | 18 430 | 120 | 0,24 | 0,17 | $2,06 \cdot 10^{-6}$ |
| | $CH_3OH$ | 18 405 | 125 | 0,39 | 0,31 | $3,75 \cdot 10^{-6}$ |

Accordingly, the experimental results considered enable one to assume that components II and III belong, apparently, to the same system of levels, while component I belongs to another, since the change in the half width for these components, on changing the solvent, occurs in opposite directions. Probably the system of levels corresponding to band I in the case of the $Er^{3+}$ ion, when it is in alcoholic solution, is lower with respect to the system of levels corresponding to bands II and III than in aqueous solution. Both systems of levels split up more strongly in a field of $CH_3OH$ molecules than in a field of $H_2O$ molecules, which leads to an increase in the force of the oscillators for all three bands in alcoholic solutions. The value of the oscillator force indicates that the bands owe their origin either to dipole transitions inside the $4f$ shell of $Er^{3+}$, or to intercombination transitions.

Resolution of the complex band of Ho at 537.0 mμ in the spectrum of aqueous and alcoholic solutions was carried out in a similar fashion. The short-wave wing of the complex band has a Gaussian shape, while on the long-wave wing in the spectra of aqueous solutions, there is a clearly defined step, beyond which there follows a very slow drop towards longer wavelengths; two peaks are visible in the spectra of alcoholic solutions (Fig. 3). Taking into account, as before, that the short-wave wing of the band is the undistorted wing of the first component, we completed its Gaussian contour, and then subtracted it from the total contour of the curve. The

short-wave wing constructed in this way by the differences in the bands also had a Gaussian shape, from this component II was determined, and then by subtraction, the third component. The latter third component was not strictly symmetrical. Its slow drop towards the long-wavelength side is possibly connected with superposition of the background, or with the presence of yet another component, separation of which was not achieved. The same parameters were determined for all the band components as in the case of $Er^{3+}$ spectra: $D_0$, $\nu_0$, $\Delta$, and S as functions of the concentration; the forces of the oscillators corresponding to them were calculated. The solutions were studied within the concentration range 0.1-4.0%. It was found, just as in the case of the $Er^{3+}$ spectrum that $\Delta$ and $\nu_0$ are constant, and are independent of the concentration, while $D_0$ and S are directly proportional to the concentration. The half widths of all three components differ little from each other.

On switching from aqueous solutions of $Ho^{3+}$ to alcoholic solutions appreciable changes in the spectrum are observed: components I, II, and III are displaced toward the long-wavelength side by 50, 25, and 25 $cm^{-1}$, respectively, while the half width and the oscillator force of bands I and II decrease by $\Delta_{H_2O}/\Delta_{MeOH} = 1.06$ and 1.95 and $f_{H_2O}/f_{MeOH} = 1.39$ and 1.80 times, respectively, and the corresponding values for band III increase $\Delta_{H_2O}/\Delta_{MeOH} = 0.97$ and $f_{H_2O}/f_{MeOH} = 0.55$. The distance between the components in the spectrum of aqueous solutions is greater than in the spectrum of alcoholic solutions: $\nu_I - \nu_{II} = 135$ $cm^{-1}$ and 105 $cm^{-1}$ and $\nu_{II} - \nu_{III} = 135$ $cm^{-1}$ and 110 $cm^{-1}$, respectively. Presumably, the regularities observed in the spectra can be explained by considering that components I and II belong to a doublet, the distance between the upper levels of which, on switching from an alocholic to an aqueous solution, increases. The forces of the oscillators corresponding to these levels increase in the stronger field of water molecules; their magnitude is of the same order as oscillator forces for forbidden dipole transitions within the $4f$-shell ($1.0 - 0.5 \cdot 10^{-5}$).

Thus a detailed and careful analysis of all the parameters of the absorption bands enables one to expose those characteristics, on the basis of which it is possible, with known accuracy, to judge the differences in the origin of bands, which would be impossible if we had restricted ourselves to the usual study of the absorption at the maximum. A study of the structure of complex bands, and of the relationships that exist between the parameters of the components and the concentration, is also important for the purposes of spectrophotometric analysis. Deviations from Beer's law, which are often observed at high concentrations of the solutions, may be caused not only by the formation of new complexes and compounds, but also by differences in behavior of individual components on changing the concentration.

The study carried out on the absorption bands, which have been chosen for analytical purposes in the spectra of aqueous and alcoholic solutions of $Er^{3+}$ and $Ho^{3+}$, has shown that differences in the characteristics of the components of a complex band have no effect on the results of spectrophotometric determinations. The position of the band in the spectrum does not depend on the concentration, while the absorption coefficient at the maximum $D_0$ is proportional to the concentration, and Beer's law is strictly obeyed within the limits investigated to 0.05 to 1.0% both in aqueous and alcoholic solutions of Ho and Er chlorides (Fig. 3).

A study was made of the effect on the experimental results of large amounts of Dy in the solution, taking as an example 5% solutions of Dy containing various amounts of erbium. It was found that Beer's law is strictly observed for these solutions also (Fig. 4).

The reproducibility of the suggested method, as determined from 10 replicate measurements, was found to be 3% for the concentration range 0.2-1.0%, and 5% for the concentration range 0.05-0.2%. The method can be recommended for the determination of Er and Ho in aqueous and alcoholic solutions containing Dy and other rare earths which do not have absorption bands in the part of the spectrum chosen for analysis.

In conclusion the authors wish to thank É. E. Vainshtein for his help in preparing this article.

## SUMMARY

A quantitative method has been developed for the spectrophotometric determination of Er and Ho in aqueous and alcoholic solutions, in the presence of Dy and other rare earths which do not have absorption bands in the spectral region in which lie the absorption bands Er $\lambda$ 522.2 m$\mu$ and Ho $\lambda$ 536.8 m$\mu$ chosen for analysis. Determinations can be carried out within the concentration limits 0.05-1.0%; the accuracy of the method is 3-5%.

An analysis of the fine structure of the complex absorption bands chosen for analysis has been carried out. It has been shown that the parameters of the individual components of a complex band change differently on replacing the aqueous surroundings of the absorbing ions by an alcoholic one.

## LITERATURE CITED


[1] P. M. Polyakov and A. K. Rusanov, Zavodskaya Lab. 23, 564 (1957).

[2] A. W. Wylie, J. Soc. Chem. Ind. 69, 143 (1950).

[3] F. Moeller and J. C. Brantley, J. Am. Chem. Soc. 72, 5447 (1950).

[4] C. K. Jorgenson, Acta Chem. Scandinavica 8, 1495 (1951).

[5] É. E. Vainshtein and I. I. Antipova-Karataeva, Zhur. Neorg. Khim. 4, 783 (1959).

[6] T. P. Kravets, Izv. Imp. Mosk. Inzh. Uchilishcha, Part 2, No. 6 (1912).

# PHOTOMETRIC DETERMINATION OF TITANIUM IN THE FORM OF A PYRIDINE-SALICYLATE COMPLEX

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The peroxide method is usually used for the determination of small amounts of titanium in steel and other alloys. Determination of titanium in the form of a peroxide compound in the presence of a large amount of iron, chromium, vanadium, and other elements requires preliminary separation of titanium in the form of its cupferronate.

A photometric method* for the determination of titanium has been published, which is based on extraction of up to 99.8% of it at pH 3 by chloroform, in the form of the compound formed between titanium sulfosalicylate and tributylammonium. Tributylammonium is, however, not readily available. The chemical characteristics of the colored ternary compound of titanium are not given in this paper.

During a study of the salicylate complexes of titanium we established that at pH 3.5-5 a complex which is anionic in character is formed. This complex forms with certain organic bases (pyridine, quinoline, pyramidone, etc.) compounds which are sparingly soluble in water, but possess considerable solubility in chloroform. The compounds are intensely colored. During visual determination of the sensitivity, the yellow color was still observable at a titanium concentration of 10 $\mu$g in 25 ml of chloroform extract. We used this technique for developing a method for the photometric determination of titanium in steel.

A more detailed study has shown** that the compound formed is the pyridine salt of titanyl salicylic acid. On the basis of the analytical results and of a number of its properties, the following formula can be suggested for this compound

$$PyH\left[(TiO)\left(\begin{array}{c}O\\ \diagup\quad\diagdown C_6H_4\\ HOOC\end{array}\right)_3\right].$$

The properties of this compound are similar to the properties of other ternary compounds formed in a system consisting of ion, metal anion, organic base.

In Fig. 1 is shown the absorption curve of a chloroform extract of the ternary complex of titanium, measured on a SF-4 spectrophotometer. To a solution containing $1 \cdot 10^{-4}$ g titanium was added 0.1 g each of sodium salicylate and the organic base. The pH of the solution prepared was adjusted to 3 and the solution extracted, the extracts were combined and then diluted with chloroform to 25 ml, after which the optical density was

* Ziegler, H., Glemser, O., Backman A. U., Z. analyt. Chem. 160, 324 (1958).
** In the press.

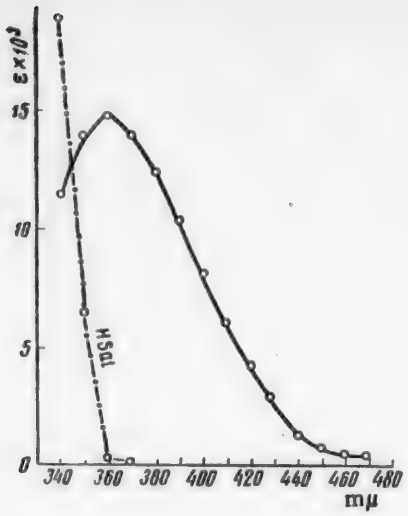


Fig. 1. Absorption curve of chloroform extracts of the pyridine-titanium salicylate complex. Titanium concentration $1 \cdot 10^{-4}$ M; layer thickness 1 cm.

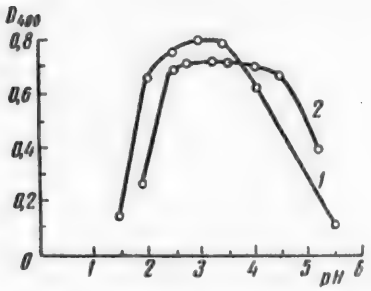


Fig. 2. Percentage extraction of the titanium-salicylate complexes with pyridine and pyramidone as a function of the pH of the aqueous phase. 1) Pyridine complex; 2) pyramidone complex; titanium concentration $1 \cdot 10^{-4}$ M.

measured. The reference solution was chloroform which had been used for extracting a corresponding control solution free from titanium. The optical characteristics of the complex change little as a function of the organic base. When the titanium is extracted once, 89-96% of it is extracted, the percentage extraction increases slightly, in the order pyridine < quinoline < pyramidone.

In order to establish the optimum pH for the extraction, a solution of titanium salicylate (25 ml) containing $1 \cdot 10^{-4}$ g of titanium and 0.1 g of sodium salicylate was prepared. To this solution was added 0.1 g of the base (pyridine, quinoline, or pyramidone), the pH was adjusted to a definite value (using indicator paper) and the solution extracted 3-4 times with 5 ml lots of chloroform. The chloroform extracts were combined and the volume made up to 25 ml with chloroform, and the solution photometrically measured at 400 mμ in a cuvette with a layer thickness of 1 cm. The pH of the aqueous phase was checked with a quinhydrone electrode.

The results obtained are shown in Fig. 2. The optical density of the extracts of the pyridine- and pyramidone-salicylate complexes of titanium is plotted on the ordinate, while the pH of the aqueous phase is plotted on the abscissa. We established separately that extracts of the pyridine-salicylate complex of titanium conform to Beer's law. The optimum conditions for the extraction of the pyridine-salicylate complex is a pH of 3-3.5, while for the quinoline- and pyramidone-salicylate complexes the pH range is wider: 2.5-4.

Photometric determination of titanium. It was established in preliminary experiments that the salicylates of quinquevalent vanadium, divalent copper, and trivalent iron form with pyridine, quinoline, and pyramidone similarly colored ternary compounds which are readily extractable by chloroform. Sexivalent chromium reacts under the same conditions to form a yellow-colored compound but only with pyramidone, this compound is also extracted by chloroform. Chromium which has been reduced by thiosulfate does not form a colored compound. Thiosulfate reduces (and combines into a complex) iron, copper, chromium, vanadium, and other elements, so that formation of the colored ternary complexes of these elements is not observed. Nickel in the presence of sodium salicylate and pyridine at a pH of 4 and 5 is partially extracted by chloroform in the form of a blue compound. At pH 3.5, nickel is not extracted by chloroform.

On the basis of the results obtained we have developed the following method for the determination of titanium in steels. 0.1-0.2 g of steel (containing 1-0.1 mg Ti) is dissolved, as usual, in sulfuric acid (1 : 9) to which nitric acid has been added. The flask is boiled to remove nitrogen oxides, it is then cooled and the contents transferred to a 50-100 ml standard flask. Ten ml of this solution is transferred to a 50 ml conical flask in which it is neutralized with $NH_4OH$ (1 : 1) solution to a pH of 1-2; 1-2 drops of 1% ammonium thiocyanate is added; this is followed by dropwise addition of a 10% solution of thiosulfate until the color of ferric thiocyanate has disappeared. 1-2 ml of a 10% solution of sodium salicylate is added; this is followed by 0.1 g pyridine (quinoline) or 5 ml of a 2% solution of pyramidone. The pH of the solution is adjusted to 3-3.5 by

Determination of Titanium in Steel

| Standard sample | Content, % | | | | | Titanium found in %, on using: | | Error in % (relative) on using: | |
|---|---|---|---|---|---|---|---|---|---|
| | Cr | Ni | Cu | V | Ti | pyridine | pyramidone | pyridine | pyramidone |
| 83-e | 0,11 | 0,09 | 0,22 | | 0,12* | 0,12 | 0,12 | 0 | 0 |
| 123a | 24,57 | 0,22 | 0,11 | | 0,26 | 0,26 | 0,27 | 0 | 3,8 |
| 123a | 24,57 | 0,22 | 0,11 | 5* | 0,26 | 0,26 | 0,27 | 0 | 3,8 |
| 52-a | 17,49 | 9,60 | 0,21 | | 0,41 | 0,41 | 0,42 | 0 | 2,4 |
| 52-a | 17,49 | 9,60 | 0,21 | 10* | 0,41 | 0,40 | — | 2,4 | — |
| 167 | 21,09 | 74,42 | 0,06 | | 2,44 | 2,40 | 2,42 | 1,4 | 0,8 |
| 167 | 21,09 | 74,42 | 0,06 | 50* | 2,44 | 2,48 | — | 1,6 | — |
| 87 | 12,55 | 0,55 | — | 2,26 | 0,12* | — | 0,12 | — | 0 |

* Added.

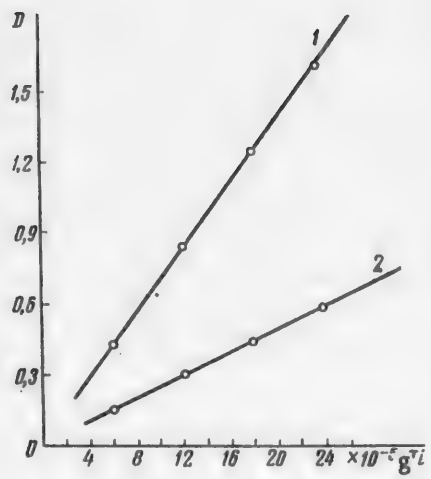


Fig. 3. Calibration curve for the determination of titanium in steel, in the form of its pyridine-salicylate complex. 1) at 400 mμ; at 430 mμ; layer thickness 1 cm.

means of ammonia (using indicator paper) and 10 ml of an acetate buffer with a pH of 3.5-3 added. The solution is transferred to a separating funnel, and is extracted 3-4 times with 4-5 ml lots of chloroform. The chloroform extracts are collected in a 25 ml flask, the volume is made up to the mark with chloroform and the optical density measured. The maximum light absorption of the compound, as is evident from Fig. 1, is found at 365 mμ; however, in this spectral region the absorption band of salicylic acid starts to appear. Accordingly, in order to avoid possible errors, and also to give a technique which is suitable for work with visual instruments, we carried out the photometric determinations at 400 or 430 mμ. At the same time, as can be seen from Fig. 1, the sensitivity increases (see also Fig. 3) at the lower wavelengths.

In Fig. 3 are shown the calibration curves for the determination of titanium in the form of its pyridine-salicylate complex. The solutions were prepared in the same way as indicated above for studying the absorption curves. The optical density was measured at 400 and 430 mμ. As is evident from the diagram, the test solutions conform to Beer's law.

The Table contains the results of determinations of titanium in several samples of steel. Determination of titanium in steel was carried out with the titanium in the form of both its pyridine-salicylate complex and its pyramidone-salicylate complex. The results given for the determination of titanium are the mean values of 6-8 determinations.

## SUMMARY

A new method has been developed for the determination of titanium in steels. It is based on the extraction of the pyridine-(or quinoline, or pyramidone) salicylate complex of titanium at a pH of 3 with chloroform. The optical density of the yellow-colored extracts is measured at 400 or 430 mμ. Interference from iron, chromium, vanadium, and other interfering elements can be eliminated by treatment with the thiosulfate prior to extraction. The sensitivity of the method is 10 μg of titanium in 25 ml of extract.

# EXTRACTION-PHOTOMETRIC DETERMINATION OF TRACES OF LEAD IN HIGH-PURITY REAGENTS

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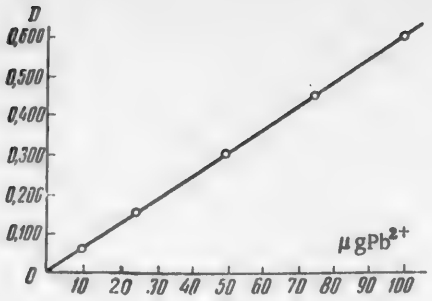
"Special purity" sodium iodide used for the preparation of crystallophosphors is controlled for its iron content and for total heavy metals, in the latter case thioacetamide in an alkaline medium is used [1]. The heavy-metals content in preparations of thallium iodide used for the activation of alkaline halide monocrystals is not controlled [2]. At the same time the content of lead which extinguishes the luminescence should not exceed $10^{-5}$ % in monocrystals [3].

The method usually used for determination of traces of lead and which involves extraction by a dithizone solution includes the use of masking agents, in particular potassium cyanide, which is toxic [4]. In individual cases, when the number of accompanying metal impurities is not large, selective determination of lead by dithizone can be effected by regulating the pH [5]. The most difficult problem is separation of lead from thallium by fractional extraction of their dithizonates in the presence of potassium cyanide, with subsequent decomposition of thallium dithizonate by potassium cyanide [4].

We have developed a method for the determination of traces of lead in thallium compounds in which interfering elements are removed by extraction. Thallium and iron are removed by extraction with oxygen-containing solvents in a hydrochloric acid medium; traces of lead, nickel, cobalt, manganese, and zinc are extracted in the form of their pyridine-thiocyanate complexes [6-9]. After removal of the macrocomponents and the microimpurities from the aqueous solution, lead diethyldithiocarbamate is extracted with chloroform. The lead content is determined by photometric measurement of the colored chloroform extract of copper diethyldithiocarbamate formed as the result of the equivalent substitution of lead ions by copper ions. The quantitative character of the exchange has been shown by a number of authors [10-13]. The behavior of sodium diethyldithiocarbamate at various pH values [14] indicates that it should be possible to use the method even at pH about 8.

A five g aliquot of thallium iodide is heated in a heat-stable beaker with 5 ml of water, 1 ml of concentrated sulfuric acid and 2 ml of concentrated nitric acid until fumes of sulfuric acid are evolved. The almost dry residue obtained is dissolved in 150 ml of hot water (when thallous sulfate is analyzed, an aliquot can be dissolved directly in water). To the solution obtained is added 10 ml of concentrated hydrochloric acid and 10 ml of hydrogen peroxide; the mixture is then slowly heated until the thallium chloride formed has dissolved completely. The solution is cooled and a further 10 ml of hydrogen peroxide added; it is then allowed to stand for 15 min in order to oxidize the thallium. Excess peroxide is removed by heating the solution and at the same time evaporating it to a volume of 2-3 ml. The solution remaining is transferred quantitatively to a 100 ml separating funnel, using 20 ml of 6 N hydrochloric acid for this purpose. The solution is extracted three times with 20 ml lots of isoamyl acetate; the organic layer is discarded. To the aqueous solution is added one drop of phenol red and the solution neutralized with ammonia until it is straw-yellow in color. Five ml of a 10% solution of ammonium thiocyanate is added next, followed by 1 ml of pyridine and 10 ml of chloroform;




Calibration curve for the determination of lead.

the solution is then extracted. The chloroform layer is discarded, while the aqueous layer is washed twice with 5 ml lots of chloroform. To the aqueous layer is added 30 ml of a mixture consisting of an ammonia-citrate buffer (pH about 8) and a 5% aqueous solution of sodium diethyldithiocarbamate in the proportion 2: 1, 10 ml of chloroform is added and the lead carbamate extracted by vigorous shaking for about 3 min. The chloroform layer is washed three times with water to free it from excess sodium diethyldithiocarbamate. For quantitative removal of traces of the chloroform extract from the aqueous wash liquors the latter are washed three times with 2-3 ml of chloroform, the chloroform washes being added to the main chloroform extract. Finally, to the extract is added 10 ml of a 0.01% solution of a copper salt in the ammoniacal-citrate buffer solution and the whole vigorously shaken for about 4 min. The yellow-colored chloroform layer is poured into a 25 ml standard flask, to this is added a few ml of chloroform used for washing the aqueous layer, after which the volume is made up to the mark with chloroform. The solution is filtered into a cuvette with a layer thickness of 5 cm and the optical density measured on a FÉK-M photocolorimeter fitted with a blue filter; the density is measured against chloroform as a reference. The optical density found during a blank run is subtracted from the optical density found for the test solution; in the blank run the solution is taken through all the operations described above using all the reagents mentioned; the lead content is then found from a calibration curve.

The calibration curve is constructed by introducing different amounts of $Pb^{2+}$ (from 2.5 to 100 μg) into the separating funnel, 30 ml of the mixture of the ammoniacal-citrate buffer* and sodium diethyldithiocarbamate, and 10 ml of chloroform are added and the procedure outlined above then followed.

The reagents used were subjected to special purification. The water was distilled, while pyridine, nitric, and hydrochloric acids were purified by distillation in pyrex apparatus; the ammonia solution (s.gr. 0.95) was prepared by saturating twice-distilled water with gaseous ammonia; cupric sulfate, ammonium thiocyanate (chemically pure grade) and sodium diethyldithiocarbamate [14] were purified by recrystallization; the mixture of the solutions of ammoniacal-citrate buffer and sodium diethyldithiocarbamate was purified by shaking with chloroform until a completely colorless chloroform layer was obtained; the hydrogen peroxide and chloroform used were "medical" grade; the sulfuric acid passed the Saval test; the sodium iodide was a highly pure preparation with a lead content of $3 \cdot 10^{-5}$ %.

The results of all the measurements were treated statistically at a confidence level of 0.95 [16]. The calibration curve (diagram) which was constructed by the method of least squares [17] for the concentration range 3 to 100 μg, the number of measurements being equal to 16, showed good conformity to Beer's law. The error in measuring D is ± 3.4% (relative).

A study was made of the possibility of determining lead in the presence in the original solution of copper, nickel, cobalt, manganese, iron, and zinc ions in amounts one thousand times greater than the lead content. It was shown that these ions are completely removed during the extraction of their pyridine-thiocyanate complexes, and that they do not interfere with lead determination (Table 1).

In order to check the method, a known amount of a lead salt was added to a solution prepared from thrice-recrystallized thallous sulfate** and containing 10 mg thallium, and the procedure outlined above followed. The lead content in μg was calculated by means of the empirical formula C = 164.5 D. Results of the statistical treatment of the data obtained [16] are given in Table 2.

The method could also be used for other thallium compounds ($Tl_2O$, $Tl_2O_3$, $Tl_2CO_3$, etc.) after treating an aliquot of the corresponding preparation with concentrated sulfuric acid.

* The buffer is prepared by neutralizing a 20% solution of citric acid with ammonia using phenol red as indicator; the neutralization is carried out to the point at which raspberry color appears.

** The lead content of the $Tl_2SO_4$ preparation did not exceed $7.2 \cdot 10^{-5}$ %.

TABLE 1

Separation of Foreign Metals during the Pyridine-Thiocyanate Extraction

| Introduced | | Optical density, D | Introduced | | Optical density, D |
|---|---|---|---|---|---|
| $Pb^{2+}$, μg | foreign metal ion, 1000 μg each | | $Pb^{2+}$, μg | foreign metal ion, 1000 μg each | |
| — | — | 0,056 | — | $Fe^{3+}$ | 0,052 |
| — | $Cu^{2+}$ | 0,048 | — | $Zn^{2+}$ | 0,058 |
| — | $Ni^{2+}$ | 0,052 | — | $Cu^{2+}$, $Ni^{2+}$, $Co^{2+}$ * | 0,053 |
| — | $Co^{2+}$ | 0,046 | 10 | — | 0,108 |
| — | $Mn^{2+}$ | 0,058 | 10 | $Cu^{2+}$, $Ni^{2+}$, $Co^{2+}$, $Mn^{2+}$, $Fe^{3+}$ * | 0,104 |

* Introduced simultaneously

TABLE 2

Determination of Lead in Thallous Sulfate (10 mg of $Tl_2SO_4$ was added to the working and control solutions)

| $Pb^{2+}$ introduced, μg | $Pb^{2+}$ found, μg | Results of statistical treatment | $Pb^{2+}$ introduced, μg | $Pb^{2+}$ found, μg | Results of statistical treatment |
|---|---|---|---|---|---|
| 5,0 | 5,4 | Dispersion | 10,0 | 9,5 | Error ± 5.6% (relative) |
| 5,0 | 4,3 | $S^2 \cdot 10^4 = 54,5$ | 25,0 | 25,0 | |
| 5,0 | 4,6 | Precision | 25,0 | 26,0 | |
| 10,0 | 9,0 | $\delta_{0,95} = \pm 0,056$ | 25,0 | 24,2 | |
| 10,0 | 9,9 | | | | |

TABLE 3

Determination of Lead in Sodium Iodide (10 g of NaI was added to the working and control solutions)

| $Pb^{2+}$ introduced, μg | $Pb^{2+}$ found, μg | Results of statistical treatment | $Pb^{2+}$ introduced μg | $Pb^{2+}$ found, μg | Results of statistical treatment |
|---|---|---|---|---|---|
| 3,0 | 3,3 | Dispersion | 5,0 | 4,9 | Error ± 5.6% (relative) |
| 3,0 | 3,0 | $S^2 \cdot 10^4 = 16$ | 5,0 | 5,3 | |
| 3,0 | 3,0 | Precision | 25,0 | 25,8 | |
| 5,0 | 5,1 | $\delta_{0,95} = \pm 0,033$ | 25,0 | 26,3 | |

The following technique was developed for the determination of lead in sodium iodide of special purity.

Ten g of sodium iodide was dissolved in 30 ml of water and the solution transferred to a 100 ml separating funnel, 3 ml of a 1% solution of sodium thiosulfate (for combining with the iodine) was added, followed by two drops of phenol red and the solution acidified with 6 N hydrochloric acid until its color is a straw-yellow. The pyridine-thiocyanate extraction was then carried out and all the subsequent operations described above carried out.

Results for the determination of lead in sodium iodide are given in Table 3.

## SUMMARY

A method has been developed for the determination of down to $6 \cdot 10^{-5}$ g of lead in thallium compounds without using potassium cyanide.

It has been shown that lead can be determined after removal of one thousand times its amount of various cations.

The method is used for the determination of down to $3 \cdot 10^{-5}$ % in sodium iodide of special purity.

## LITERATURE CITED

[1] VTU, MKhP, No. RU 1151-56.

[2] VTU, MKhP No. 3380-52.

[3] A. V. Moskvin, Cathodoluminescence [in Russian] (Gostekhizdat, 1949) p. 109.

[4] E. B. Sandell, Colorimetric Determination of Traces of Metals [Russian translation] (Goskhimizdat, 1949) p. 427.

[5] Yu. Yu. Lur'e and Z. V. Nikolaeva, Zavodskaya Lab. 23, 652 (1957).

[6] Yu. Yu. Lur'e and A. G. Ginzburg, Zavodskaya Lab. 7, 2 (1938).

[7] V. I. Kuznetsov, Uspekhi Khim. 23, 654 (1954).

[8] A. K. Babko and M. M. Tananaiko, Ukr. Khim. Zhur. 24, 499 (1958).

[9] Yu. Yu. Lur'e, Zavodskaya Lab. 11, 273 (1945).

[10] H. Bode and J. K. Tusche, Z. Analyt. Chem. 157, 414 (1957).

[11] J. Eckert, Z. Analyt. Chem. 155, 23 (1957).

[12] V. Vasak and V. Sedivec, Chem. Listy 45, 437 (1951).

[13] V. Sedivec and V. Vasak, Chem. Listy 46, 607 (1952).

[14] H. Bode, Z. Analyt. Chem. 142, 414 (1954).

[15] J. Kolmeschate and R. W. Stern, Chem. Weekbl. 45, 733 (1949).*

[16] N. P. Komar', Zhur. Anal. Khim. 7, 325 (1952).**

[17] W. J. Youden, Analyt. Chem. 19, 946 (1947).

*Not mentioned in the Russian text – Publisher's note.

**Original Russian pagination. See C. B. translation.

# COMPLEXONOMETRIC DETERMINATION OF BISMUTH AND LEAD IN BISMUTH-LEAD ALLOYS

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Bismuth-lead alloys, in particular eutectic alloys, are used in nuclear technics as a coolant [1-3]. The chemical methods used for determining lead and bismuth in each other's presence are laborious and are not accurate enough. Thus, the well-known chromate method of determining lead at high bismuth contents, as a rule, gives high results for lead as a result of coprecipitation of bismuth. The error amounts to 1-3%.

The achievements of complexonometry in recent years lead one to suggest that of the chemical methods of analyzing bismuth-lead alloys, a complexonometric analysis would appear to be the most convenient with respect to the speed with which it can be carried out and with respect to the accuracy. Moreover, in contrast to other methods, successive direct determination of both components on one aliquot would appear to be possible. Complexonometric titration of various combinations of elements [4], including the pair Bi: Pb [5] is possible. Bismuth can be titrated directly with sodium ethylenediaminetetracetate (EDTA-Na) at pH 1-2, and lead at pH 4-6 [4, 6, 7]. In these cases it is expedient to use metal indicators which react with both bismuth and lead at the corresponding pH values. Such indicators include: pyrocatechol violet [8-11], pyrogallol red [12], bromopyrogallol red [13], methyl thymol blue [14, 15],* xylenol orange [5, 15, 16], hematoxylin [17, 18], 1(2-pyridylazo)-2-naphthol [7,19].**

Having tested all the indicators mentioned we settled on xylenol orange as the most sensitive one and the one giving the most contrasting color change: raspberry-red to yellow for bismuth and raspberry to lemon-yellow for lead.

As a result of work which we carried out we have developed a direct complexonometric method for the determination of the components of bismuth-lead alloys using xylenol orange as metal indicator; this method is superior to current methods in accuracy and rapidity.

The method has been checked on synthetic mixtures containing various ratios of bismuth and lead, analysis being carried out both by titrations of aliquots of solutions.***

As the results in Table 1 show, successive determination of bismuth and lead gives satisfactory results. As a rule, the error does not exceed the permissible error for titrimetric methods of analysis. Moreover, the method gives reliable results over a fairly wide range of ratios of Bi to Pb (1: 10 to 10: 1).

Experimental procedure. Titration of aliquots. An aliquot of the alloy weighing about 0.1 g is placed in a 250 ml conical flask, 5-7 ml of nitric acid (1: 3) is added and the flask covered with a watch glass, the flask is heated on a sand bath until the alloy has completely dissolved (5-10 min); the solution is then diluted to

* The article by A. N. Korolev and M. K. Koichev [15] was published when we had finished our work.

** For a review on the use of complexonometric indicators, see [19].

*** Both titration of aliquots of solutions and titration of aliquots of sample gave almost equally accurate results.

TABLE 1

Determination of Bismuth and Lead in Synthetic Mixtures (25 ml aliquots from a 250 ml solution were taken for analysis)

| Bismuth | | | Bi : Pb | Lead | | |
|---|---|---|---|---|---|---|
| introduced, g | found, g | error, % (relative) | | introduced, g | found, g | error, % (relative) |
| 0,8037 | 0,8036 | —0,012 | 1 : 1 | 0,7998 | 0,7998 | 0,00 |
| 0,8068 | 0,8067 | —0,012 | | 0,8047 | 0,8029 | —0,22 |
| 0,8111 | 0,8010 | —0,012 | | 0,8008 | 0,8009 | +0,013 |
| 0,8056 | 0,8047 | —0,11 | | 0,8019 | 0,8009 | —0,13 |
| 0,8097 | 0,8099 | +0,025 | | 0,8127 | 0,8123 | —0,037 |
| 0,8078 | 0,8078 | 0,00 | 10 : 1 | 0,0753 | 0,0752 | —0,13 |
| 0,7990 | 0,7994 | +0,05 | | 0,0745 | 0,0746 | +0,13 |
| 0,8138 | 0,8136 | —0,025 | | 0,0642 | 0,0642 | 0,00 |
| 0,0816 | 0,0815 | —0,12 | 1 : 10 | 0,8101 | 0,8107 | +0,07 |
| 0,0894 | 0,0898 | +0,45 | | 0,7999 | 0,7998 | —0,012 |
| 0,0888 | 0,0888 | 0,00 | | 0,7987 | 0,7988 | +0,013 |

TABLE 2

Analysis of Various Samples of Alloys (titration of aliquots of solutions; in the first six experiments 50 ml aliquots from a 250 ml solution were taken, while in the remainder 20 ml aliquots were taken from a 250 ml solution)

| Sample No. | Wt. of aliquot, g | Bismuth | | | | Lead | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | vol. of 0.01 M EDTA-Na used for titrating Bi, ml | Bi found, % | mean | deviation from the mean | vol. of 0.01 M EDTA-Na solution used for titrating Pb, ml | Pb found, % | mean | deviation from the mean |
| 22 (turnings) | 0,8063 | 42,83 | 55,51 | 55,53 | —0,02 | 34,60 | 44,46 | 44,31 | +0,15 |
| | 0,8053 | 42,75 | 55,48 | | —0,05 | 34,35 | 44,20 | | —0,11 |
| | 0,8026 | 42,70 | 55,60 | | +0,07 | 34,30 | 44,28 | | —0,03 |
| 25 (turnings) | 0,8081 | 43,00 | 55,60 | 55,59 | +0,01 | 34,50 | 44,23 | 44,18 | +0,05 |
| | 0,8053 | 42,80 | 55,54 | | —0,05 | 34,40 | 44,26 | | +0,08 |
| | 0,8151 | 43,40 | 55,64 | | +0,05 | 34,65 | 44,04 | | —0,14 |
| 5 (sprigs) | 0,8637 | 19,60 | 59,29 | 59,03 | +0,26 | 13,60 | 40,78 | 40,79 | —0,01 |
| | 0,8250 | 18,60 | 58,90 | | —0,13 | 13,00 | 40,81 | | +0,02 |
| | 0,8381 | 18,90 | 58,92 | | —0,11 | 13,20 | 40,79 | | 0,00 |
| 6 (sprigs) | 0,8186 | 18,30 | 58,40 | 58,43 | —0,03 | 13,10 | 41,45 | 41,50 | —0,05 |
| | 0,8304 | 18,60 | 58,52 | | +0,09 | 13,30 | 41,48 | | —0,02 |
| | 0,8416 | 18,80 | 58,36 | | —0,07 | 13,51 | 41,58 | | +0,08 |

50-60 ml with distilled water and 50-100 mg of urea added for preventing the nitrogen oxides from affecting the indicator, the pH is adjusted to 0.5-1.5 with ammonia (1 : 1) using universal indicator paper, 2-3 drops of a 0.5% aqueous solution of xylenol orange * is added and the bismuth titrated with 0.01 M EDTA-Na** until the color changes from raspberry-red to yellow. The volume of EDTA-Na solution used for titrating the bismuth is noted and the buret refilled.

To the flask is next added 10-15 ml of a 25% solution of urotropine (the pH is thereby adjusted to 4.5-5.5) and the lead titrated until the color changes from raspberry to lemon-yellow.

*The 0.5% solution of xylenol orange is prepared as follows: 0.5 g of xylenol orange is dissolved in distilled water in a standard flask, 0.5 ml of hydrochloric acid (1 : 1) is added and the volume made up with water to 100 ml. The precipitate which appears after 4-5 days is filtered off. The indicator solution prepared in this way keeps for a long time. A 0.5% aqueous-alcoholic (1 : 1) solution of xylenol orange can also be used.

**In our work we used a 0.01 M solution of EDTA-Na prepared by dissolving the exact amount of the preparation. It is best to standardize the EDTA-Na solution against a solution of pure metallic lead [20].

Fifteen samples of bismuth-lead alloys have been analyzed by this method. The results obtained for some of the samples are given in Table 2.

The complexonometric method of determining the components of bismuth-lead alloys has the advantages of speed and accuracy over the chromate and other methods in use at present. The analysis can be speeded up even further, if the lead content is not determined directly but is calculated by difference.

In a six-hour working day it is possible to carry out up to 30 analyses of alloy samples (using titration of aliquots of the samples) for both components, while on titrating aliquots of solutions, up to 20 analyses can be carried out.

The mean experimental error for ten bismuth determinations is a) 0.11% (absolute) on titrating aliquots of sample; b) 0.08% (absolute) on titrating aliquots of solutions.

The mean experimental error for determination of lead is: a) ± 0.07% on titrating aliquots of sample and b) ± 0.06% for titration of aliquots of solutions. The error of a single determination is 0.2-0.3% relative.

## SUMMARY

A method is described for the successive complexonometric determination of the components of bismuth-lead alloys in a nitric acid solution, using xylenol orange as indicator. The accuracy of the method is very high; for an approximately equal weight ratio of Bi and Pb the error of a single determination of each component does not exceed 0.2-0.3% (relative). In a six-hour day it is possible to carry out 20-30 analyses for both components.

## LITERATURE CITED

[1] Atomic Energy, A Concise Encyclopedia [in Russian] (Bol'shaya Entsiklopediya Izd., Moscow, 1958) p. 425.

[2] Reactor Construction and the Theory of Reactors, Reports of the Soviet Delegation at the First Geneva Conference on the Peaceful Uses of Atomic Energy (Goskhimizdat, Moscow, 1955) p. 143.

[3] P. A. Andreev, A. A. Kanaev, and E. D. Fedorovich, Liquid-Metal Coolants for Nuclear Reactors [in Russian] (Sudpromgiz, Leningrad, 1959) p. 106.

[4] R. Pribil, Complexons in Chemical Analysis [Russian translation from Czech] (IL, Moscow, 1955).

[5] I. Körbl and R. Přibil, Chemist-Analyst. 45, 102 (1956).

[6] Complexometry, Collection of Translations (Goskhimizdat, Moscow, 1958).

[7] A. I. Busev, Zhur. Anal. Khim. 12, 386 (1957).*

[8] M. Malat, V. Suk, and O. Ryba, Coll. of Czechoslov. Chem. Commun. 19, 258 (1954).

[9] J. Cifka, M. Malat, and V. Suk, Coll. of Czechoslov. Chem. Commun. 21, 412 (1956).

[10] V. A. Zaitsev, Aptech. Delo 8, 76 (1959).

[11] G. Chiogolya et al., Aptech. Delo 8, 67 (1959).

[12] V. Suk, M. Malat, and A. Jenickova, Coll. of Czechoslov. Chem. Commun. 21, 418 (1956).

[13] V. Suk and M. Malat, Coll. of Czechoslov. Chem. Commun. 21, 1257 (1956).

[14] I. Körbl and R. Přibil, Coll. of Czechoslov. Chem. Commun. 23, 873 (1958).

[15] A. N. Korolev and M. K. Koichev, Zavodskaya Lab. 25, 546 (1959).

[16] I. Körbl and R. Přibil, Chem. Listy 51, 667 (1957).

[17] A. I. Cherkesov and A. S. Mel'nikova, Zavodskaya Lab. 25, 140 (1959).*

[18] Chemical Reagents and Preparations (Edited by V. I. Kuznetsov) [in Russian] (Goskhimizdat, Moscow, 1953) p. 273.

[19] A. I. Busev and A. G. Petrenko, Zavodskaya Lab. 24, 1449 (1958).

[20] I. Vřeštal, I. Havlíř, I. Bradstell, and S. Kotrlý, Coll. of Czechoslov. Chem. Commun. 24, 360 (1959).

* Original Russian pagination. See C. B. Translation.

# COMPLEXONOMETRIC DETERMINATION OF QUADRIVALENT PLUTONIUM USING ARSENAZO AS INDICATOR

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Very few titrimetric methods are known for the determination of plutonium; they have all been developed for trivalent plutonium and are applicable to only relatively pure solutions. Thus, Koch's cerimetric method [1] is not suitable in the presence of uranium and iron, while Milner's complexonometric method [2] was developed only for the determination of $Pu^{III}$ in the solutions obtained on dissolving the metal in hydrochloric acid.

Methods of determining plutonium in its most usual valence state of four would be of considerably greater interest. Fritz [3] has described the titration of thorium with EDTA-Na using arsenazo as an indicator at pH 1.7-3.0; this same reaction occurs with yttrium, lanthanum, and other rare earths at pH 6-10, but with calcium and magnesium in strongly alkaline media only. Taking into account the similarity between quadrivalent plutonium and thorium, as well as the properties of arsenazo [4] and the conditions under which it interacts with many cations [5], it was hoped that it would be possible to make successful use of EDTA-Na and arsenazo for the determination of $Pu^{IV}$ in the presence of uranium, lanthanum, americium, chromium, etc.

From the work of Foreman and Smith [6] it is known that $Pu^{IV}$ interacts with EDTA-Na in the proportion 1:1 to form a compound which is stable even in strongly acid solutions (1 N $HNO_3$) in which the complexes of $UO_2^{2+}$, $La^{3+}$, and many other cations dissociate completely.

Experimental. Reagents: 1) the stock $Pu^{IV}$ solution (about 0.01 M) was obtained by dissolving the pure metal in hydrochloric acid; the solution was evaporated three times to dryness with sulfuric acid, and the residue dissolved in 0.5 N $HNO_3$. The solution was standardized gravimetrically.

2) The EDTA-Na solution with a concentration of about 0.005 M was prepared by dissolving 1.86 g of the purified preparation in one liter of water. It was standardized against 0.190 M calcium chloride solution [7].

3) The indicator solution was a solution of 0.4 g of arsenazo in 100 ml water.

$Pu^{IV}$ ions form a blue-violet colored compound with arsenazo; addition of excess EDTA-Na causes the color to change to rose. The definition of the endpoint depends on the acidity of the solution. Accordingly, the first series of experiments was designed to establish the optimum acidity (Table 1).

The color change was most clearly defined and the minimum error was obtained at an acidity of 0.1-0.2 N, at a plutonium concentration of about 0.1-0.2 mg/ml, and for an amount of indicator equal to 10-20 drops for 40-100 ml of the solution being titrated.

At low acidities the errors increase, probably as a result of hydrolysis and polymerization of plutonium ions; at high acidities (> 0.3 N) the colors (blue) indicate a relative decrease in the stability of the complex of plutonium with EDTA-Na.

TABLE 1

| $Pu^{IV}$ taken mg | Initial acidity, N | Final volume, ml | No. of drops of the indicator | Amount of 0.0051 M EDTA-Na solution used, ml | Pu, found | Error | |
|---|---|---|---|---|---|---|---|
| | | | | | | mg | % |
| 2,63 | 0,04 | 100 | 10 | 1,70 | 2,07 | −0,56 | −21,2 |
| 5,26 | 0,05 | 160 | 20 | 3,92 | 4,75 | −0,51 | −9,6 |
| 2,63 | 0,05 | 80 | 12 | 2,02 | 2,47 | −0,16 | −6,1 |
| 5,26 | 0,08 | 100 | 10 | 4,26 | 5,20 | −0,06 | −1,1 |
| 2,63 | 0,08 | 50 | 10 | 2,13 | 2,60 | −0,03 | −1,1 |
| 2,63 | 0,10 | 40 | 5 | 2,14 | 2,61 | −0,02 | −0,8 |
| 2,63 | 0,10 | 40 | 6 | 2,16 | 2,63 | 0 | 0 |
| 5,26 | 0,10 | 80 | 12 | 4,28 | 5,22 | −0,04 | −0,8 |
| 2,63 | 0,10 | 40 | 8 | 2,16 | 2,63 | 0 | 0 |
| 2,63 | 0,20 | 20 | 12 | 2,18 | 2,64 | +0,01 | +0,4 |
| 2,63 | 0,20 | 20 | 8 | 2,14 | 2,61 | −0,02 | −0,8 |
| 5,26 | 0,20 | 40 | 10 | 4,31 | 5,25 | −0,01 | −0,2 |
| 5,26 | 0,20 | 40 | 10 | 4,30 | 5,24 | −0,02 | −0,4 |
| 2,63 | 0,30 | 15 | 6 | 2,19 | 2,67 | +0,03 | +1,1 |
| 5,26 | 0,30 | 25 | 10 | 4,40 | 5,37 | +0,11 | +2,1 |
| 2,63 | 0,40 | 10 | 14 | 2,43 | 2,96 | +0,33 | +12,5 |
| 5,26 | 0,6 | 15 | 6 | 4,80 | 5,85 | +0,59 | +11,2 |
| 10,52 | 0,15 | 110 | 20 | 8,59 | 10,48 | −0,04 | −0,4 |
| 13,15 | 0,18 | 100 | 28 | 10,76 | 13,12 | −0,03 | −0,3 |
| 1,35 | 0,15 | 10 | 6 | 1,10 | 1,35 | 0 | 0 |
| 21,04 | 0,12 | 180 | 40 | 17,14 | 20,91 | −0,14 | −0,66 |
| 26,19 | 0,18 | 80 | 23 | 21,32 | 26,02 | −0,17 | −0,65 |
| 25,56 | 0,15 | 100 | 25 | 11,48 | 25,24 | −0,32 | −1,2 |

TABLE 2

| $Pu^{IV}$ taken, mg | Introduced, mg | | Initial acidity, N | Initial volume, ml | No. of drops of the indicator | Amount of 0.0051 M EDTA-Na solution used, ml | Pu found, mg | Error | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | mg | % |
| 2,63 | $La^{3+}$ | 8,5 | 0,12 | 40 | 12 | 2,14 | 2,61 | −0,02 | −0,8 |
| 5,26 | $La^{3+}$ | 18 | 0,15 | 60 | 12 | 4,28 | 5,22 | −0,04 | −0,8 |
| 2,63 | $UO_2^{2+}$ | 10 | 0,15 | 30 | 10 | 2,18 | 2,64 | +0,01 | +0,4 |
| 5,26 | $UO_2^{2+}$ | 40 | 0,15 | 60 | 15 | 4,28 | 5,22 | −0,04 | −0,8 |
| 1,42 | $UO_2^{2+}$ | 100 | 0,15 | 20 | 15 | 1,18 | 1,44 | +0,02 | +1,4 |
| 1,42 | $UO_2^{2+}$ | 200 | 0,15 | 30 | 25 | 1,22 | 1,48 | +0,06 | +4,2 |
| 1,42 | $UO_2^{2+}$ | 100 | 0,12 | 50 | 15 | 1,14 | 1,39 | −0,03 | −2,1 |
| 1,42 | $UO_2^{2+}$ | 200 | 0,12 | 50 | 23 | 1,14 | 1,39 | −0,03 | −2,1 |
| 2,63 | $Fe^{3+}$ | 10 | 0,15 | 30 | 15 | 4,9(?) | ? | — | — |
| 5,26 | $Fe^{3+}$ | 5 | 0,15 | 60 | 15 | 4,9(?) | ? | — | — |
| 2,63 | $Cr^{3+}$ | 4 | 0,15 | 30 | 10 | 2,16 | 2,63 | 0 | 0 |
| 2,63 | $Cr^{3+}$ | 10 | 0,15 | 30 | 10 | 2,18 | 2,65 | +0,02 | +0,8 |
| 2,63 | $Pb^{2+}$ | 8 | 0,12 | 35 | 10 | 2,14 | 2,61 | −0,02 | −0,8 |
| 2,63 | $Ni^{2+}$ | 5 | 0,15 | 30 | 10 | 2,16 | 2,63 | 0 | 0 |

The effect of other cations on the determination of $Pu^{IV}$ depends on the stability of their compounds with ethylenediaminetetracetic acid and with arsenazo at the given acidity. The low stability of the complexonates of Ca, Mg, Zn, Al, Cd, and Mn in acid media ensures that they will have little effect; on the other hand, Th, Zr, and $U^{IV}$, which under these conditions give bright colors with arsenazo, should interfere even at low concentrations of these elements. Table 2 contains results for the determination of plutonium in the presence of the elements which usually accompany it.

TABLE 3

(Acidity 0.15 N)

| $Pu^{IV}$ taken, mg | $Fe^{3+}$ introduced, mg | Initial volume, ml | No. of drops of the indicator | Amount of 0.0051 M EDTA-Na solution used, ml | Pu found, mg | Error | |
|---|---|---|---|---|---|---|---|
| | | | | | | mg | % |
| 2,91 | 0,045 | 15 | 8 | 2,39 | 2,91 | —0— | —0— |
| 2,97 | 0,045 | 15 | 8 | 2,44 | 2,97 | —0— | —0— |
| 2,91 | 0,09 | 15 | 8 | 2,39 | 2,91 | —0— | —0— |
| 2,97 | 0,09 | 15 | 8 | 2,46 | 3,00 | +0,03 | +1,0 |
| 2,97 | 0,09 | 15 | 8 | 2,44 | 2,97 | —0— | —0— |
| 2,91 | 0,15 | 15 | 8 | 2,40 | 2,92 | +0,01 | +0,3 |
| 2,97 | 0,15 | 15 | 8 | 2,50 | 3,05 | +0,08 | +2,8 |
| 2,91 | 0,23 | 20 | 10 | 2,46 | 3,00 | +0,09 | +3,0 |
| 2,97 | 0,23 | 20 | 10 | 2,55 | 3,11 | +0,14 | +4,9 |
| 2,84 | 0,40 | 15 | 10 | 2,76? | ? | — | — |

Experiments showed that uranyl ions even when present in amounts which were 140 times that of plutonium, do not rule out the possibility of determining plutonium. Of the elements which usually accompany plutonium, only $Fe^{3+}$ ions interfere.

Iron can be tolerated in amounts of up to 3-4% of the plutonium at concentrations up to 1 mg in 100 ml (Table 3).

The titration conditions are as follows: amount of plutonium 2-20 mg, volume of solution 40-100 ml, acidity 0.1-0.2 N, indicator — 0.4% solution of arsenazo — 10-20 drops, EDTA-Na concentration 0.005-0.01 M. The endpoint can be conveniently established by means of a "reference" solution, which is a solution of the indicator under the same conditions of concentration and acidity.

## SUMMARY

A method for determining $Pu^{IV}$ is described; it is based on titration with 0.01-0.005 M solution of sodium ethylenediaminetetracetate (EDTA-Na) in an acid medium (0.1-0.2 N $HNO_3$ or HCl), using arsenazo I as an indicator. $La^{3+}$, $UO_2^{2+}$, $Cr^{3+}$, $Pb^{2+}$ and $Ni^{2+}$ do not interfere. $Fe^{3+}$ must not be greater than 3-4% of the Pu content.

## LITERATURE CITED

[1] C. W. Koch, The Transuranium Elements. Ed. G. T. Seaborg, Part II, paper 17, 4, 1949.

[2] C. W. C. Milner and J. L. Woodhead, Analyst 81, 427 (1956).

[3] J. S. Fritz, Anal. Chem. 30, 1111 (1958).

[4] V. I. Kuznetsov, Zhur. Anal. Khim. 13, 220 (1958).*

[5] A. F. Kuteinikov, Zavodskaya Lab. 24, 1050 (1958).

[6] T. K. Foreman and T. D. Smith, J. Chem. Soc. 1752 (1957).

[7] G. B. Styunkel' and E. M. Yakimets, Zavodskaya Lab. 24, 23 (1958).

* Original Russian pagination. See C. B. Translation.

# POLAROGRAPHIC DETERMINATION OF TUNGSTEN*

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Separate polarographic determination of tungsten and molybdenum is of considerable interest, since they interfere with each other in the same supporting electrolyte; moreover, tungsten frequently does not give a wave in media in which molybdenum gives a clearly defined wave [1].

Data on the polarography of tungsten is very scant because $W^{IV}$ is not reduced in either neutral or alkali media, although it is known to be reduced in hydrochloric acid. Lingane and Small [2] have studied the various oxidation states of tungsten in hydrochloric acid polarographically. Kolthoff and Parry [3] have observed a tungsten kinetic wave in the presence of hydrogen peroxide; the wave is not controlled by diffusion. Souchay [4] has made a polarographic study of various tungstates and heteropoly acids of tungsten. Von Stackelberg et al [5] have determined tungsten in steel using 9 N hydrochloric acid as supporting electrolyte. Recently, Meites [6] observed a well-defined tungsten wave in phosphoric acid. Reichen [7] has also used tartaric acid for the determination of the tungsten content of rocks.

During a search for a common electrolyte which would give clearly defined waves for $Mo^{VI}$ and $W^{VI}$, it was noticed that in the presence of oxalic acid, under certain conditions, two clearly defined waves which are characteristic of the elements indicated are formed. Moreover, it was established that the oxalate ion prevents precipitation of the hydrated oxide of tungsten. The results obtained were used for the successive polarographic determination of molybdenum and tungsten in one solution. In addition it was also found possible to carry out separate determination of iron and tungsten.

Experimental. The polarograms were recorded at 25 ± 0.1° on a Leeds and Northrup electrochemograph type E. The reference electrode (a saturated calomel electrode) was connected to the electrolyzer via a potassium chloride – agar-agar bridge. The value of $m^{2/3} \cdot t^{1/6}$ for the capillary used varied in various experiments, since the drop time was not the same, while the weight of a mercury drop at 25° in distilled water, without an applied potential, was 7.568 mg. The pH was measured by means of a Beckman pH-meter.

The stock sodium tungstate solution was prepared by dissolving an aliquot of the chemically pure preparation in distilled water, the tungsten content was checked gravimetrically by the benzidene method.

Sodium oxalate (0.2 M solution) was used as complexing agent and as a supporting electrolyte for obtaining the tungsten waves. The pH of the solutions was regulated by addition of dilute sulfuric acid. The gelatin concentration was kept constant at 0.005%.

Characteristics of the polarographic waves. Preliminary studies were carried out with 0.2 M sodium oxalate containing 0.005% gelatin as maximum suppressor, and appropriate amounts of tungstate solution. The pH of the solution was altered by addition of dilute sulfuric acid. Polarographic waves only appeared at pH 2.0 (Table 1), but the wave height was so small that it could not be used for analytical purposes. On decreasing

* Translated from English by Z. I. Podgaiskaya.

TABLE 1

Effect of the pH of the Solution on the Polarography of Tungsten

| pH | $E_{1/2}$ (saturated calomel electrode) |
|---|---|
| 8,5 | Not reduced |
| 4,5 | Ditto |
| 3,0 | Ditto |
| 2,0 | Very small wave |
| 0,8 | —0,625 |
| 0,5 | —0,61 |
| 0,05 | —0,57 |

TABLE 2

Effect of Oxalate Concentration on the Polarography of Tungsten

| pH | Oxalate concentration, M | $E_{1/2}$ (saturated calomel electrode) |
|---|---|---|
| 0,7 | 0,5 | —0,62 |
| 0,8 | 0,25 | —0,615 |
| 0,6 | 0,20 | —0,62 |
| 0,6 | 0,125 | —0,61 |
| 0,6 | 0,10 | —0,62 |
| 0,5 | 0,05 | —0,62 |

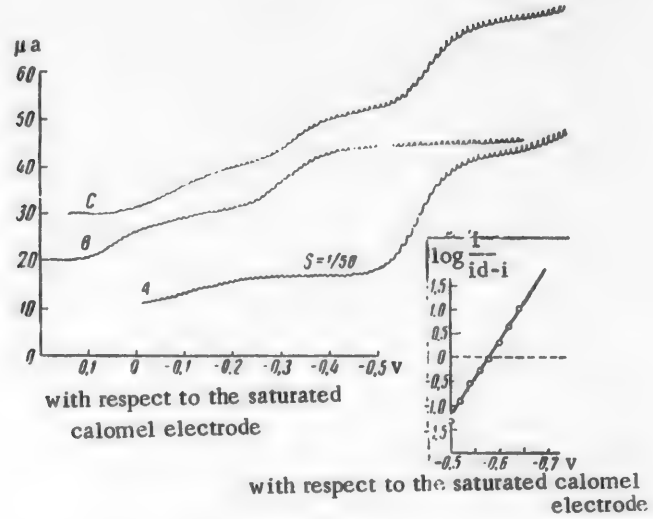


Fig. 1. Tungsten polarogram. Drop-formation time 3/5 sec; A) tungsten wave (5.95 mM) in an oxalate medium; B) molybdenum wave (2.33 mM) in an oxalate medium; C) polarogram of tungsten and molybdenum when the two are present together.

the pH further, better results were obtained and the waves were clearly defined. However, the half-wave potential was shifted toward more negative values on increasing the pH. This gives a basis for assuming that the oxalate complex of tungsten is more stable at the higher pH values, and that its stability is dependent on the acidity of the solution.

The half-wave potential remains constant and is independent of oxalate concentration within the limits 0.05-0.5 M (Table 2). However, well-defined waves appear in a medium of 0.2 M oxalate solution in the presence of 0.005% gelatin at a pH equal to or less than 1.0. When the polarograms were being recorded it was observed that the residual current increased when tungsten was present in solution, probably as a result of partial adsorption of tungsten anions on the mercury drop. This was confirmed by the fact that the residual current remained constant and was independent of the tungsten concentration.

The electrode reaction is reversible (Fig. 1). The wave was obtained in a solution containing 5.95 mM tungsten, 0.2 M sodium oxalate, and 0.005% gelatin as maximum suppressor. The relation between log $i/(i_d - i)$ and E is shown in Fig. 1. In accordance with the equation

$$E = E_{1/2} - \frac{0,059}{n} \lg \frac{i}{i_d - i}$$

TABLE 3

Diffusion Current Constants

| W concentration mM | $i_d$ (observed) | $i_d$ after correction for $i_d - i_{da}$ | $i_d / Cm^{2/3} t^{1/6}$ | I (corrected) |
|---|---|---|---|---|
| 1,19 | 1,0 | 3,0 | 0,408 | 1,22 |
| 2,38 | 3,25 | 5,25 | 0,663 | 1,07 |
| 3,57 | 6,0 | 8,0 | 0,816 | 1,08 |
| 4,76 | 8,5 | 10,5 | 0,867 | 1,07 |
| 5,95 | 11,5 | 13,5 | 0,938 | 1,10 |
| 7,14 | 14,0 | 16,0 | 0,952 | 1,12 |
| 8,33 | 17,0 | 19,0 | 0,991 | 1,13 |
| 9,529 | 19,25 | 21,25 | 0,981 | 1,08 |
| 10,72 | 22,0 | 24,0 | 0,996 | 1,08 |
| 11,91 | 25,0 | 27,0 | 1,02 | 1,10 |
| 13,1 | 28,0 | 30,0 | 1,03 | 1,11 |
| 14,29 | 30,0 | 32,0 | 1,02 | 1,09 |
| 15,48 | 33,0 | 35,0 | 1,01 | 1,10 |
| | | | Mean | 1,1±0,03 |

TABLE 4

Determination of Tungsten and Molybdenum in Each Other's Presence

| $W^{VI}$ added, mM | $W^{VI}$ found, mM | $Mo^{VI}$ added, mM | $Mo^{VI}$ found, mM |
|---|---|---|---|
| 11,91 | 11,91 | — | — |
| 9,53 | 9,52 | 1,16 | 1,16 |
| 7,14 | 7,25 | 2,33 | 2,28 |
| 4,76 | 4,76 | 3,5 | 3,48 |
| 2,38 | 2,42 | 4,6 | 4,66 |

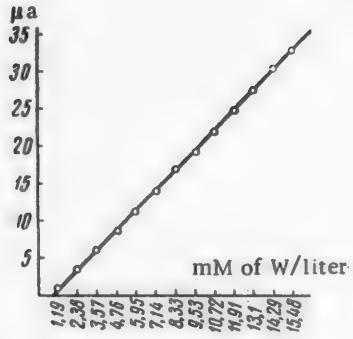


Fig. 2. Calibration curve for tungsten.

the experimental points fall on a straight line with a slope of 0,064 v. This corresponds to a one-electron transfer during reduction.

The diffusion current is directly proportional to tungsten concentration within the limits 1.19-16.67 mM. In more concentrated tungsten solutions, in the presence of oxalate ions, addition of gelatin caused the solution to become turbid, but did not affect the value of the diffusion current or the character of the wave. At higher acidities the limiting current is not very well expressed as a result of the liberation of hydrogen at the higher positive potentials.

The calculated constants of the diffusion current are given in Table 3. They decrease with decreasing tungsten concentration, but, as mentioned above, the values of the diffusion current are linearly related to the tungsten concentration. This unusual behavior may be explained by the calibration curve (Fig. 2), from which it follows that the diffusion current observed is only proportional to the tungsten concentration, while its actual value can be determined from the equation

$$i_d = IC + i_{da},$$

where $i_d$ is the observed diffusion current, I is the constant of the diffusion current, C is the concentration of the reduced tungsten ion (M), and $i_{da}$ is the adsorption current in $\mu$A. Thus, the value of the adsorption current which leads to an increase in the residual current, as determined by the curve, is 2.0 $\mu$A. This assumption is confirmed further by the fact that the mean increase in the residual current for all the tungsten concentrations studied is constant, i.e., equal to 2.0 $\mu$A. A further confirmation of this conclusion is given by experimental observations which show that on addition of any other ion which is reduced prior to the appearance of the adsorption current, the value of 2.0 $\mu$A is added to the actual height of the wave on the tungsten polarogram.

The diffusion coefficient of tungsten was calculated after applying the correction indicated above to the observed value of $i_d$ and by substituting the values obtained in this way in the equation

$$I = 605n\sqrt{D}.$$

The diffusion coefficient of the tungsten ion proved to be $3.3 \cdot 10^{-2}$ cm$^2$/sec. This value, obviously, is considerably higher than the value for the chromate ion; doubtless, tungsten is present in solution in the form of its oxalate complex. Since the constant of the diffusion current has a constant value, obviously, the extent of polymerization does not change on increasing the oxalate ion concentration.

Sexivalent molybdenum [8] is also reduced on a dropping-mercury electrode under the same experimental conditions as those for which clearly defined tungsten waves appear, and these waves do not interfere with each other. The results obtained were therefore used for the separate determination of $Mo^{VI}$ and $W^{VI}$. It was observed that the first molybdenum wave is suppressed in the presence of tungsten ions, but the latter do not affect the over-all molybdenum wave. The results obtained are given in Table 4. A correction was applied to the diffusion current for the wave of the residual current obtained at the same potential value at which the wave height of molybdenum was calculated.

The presence of chlorides, sulfates, and bisulfates of the alkali metals does not affect the tungsten polarogram. Nitrate ions lead to an increase in wave height but do not distort its shape. Probably, the current increases as the result of a catalytic reduction of nitrate ions under the experimental conditions; nitrate ions should therefore be absent.

The possibility of determining tungsten in steel was studied. In this connection the effect of iron, nickel, chromium, manganese, and vanadium ions on the tungsten wave was examined.

Iron is reduced in 0.2 M oxalic acid to give a well-defined wave. Although the value of $E_{1/2}$ for iron is strongly dependent on pH, while the wave height is dependent on the photochemical action of light [9], the half-wave potential of iron is far removed from that of tungsten. Use can be made of this fact in recording polarograms for solutions containing tungsten and iron.

Chromium, manganese, and nickel ions are not reduced under the conditions mentioned above, accordingly, the iron and tungsten waves are readily distinguishable. Iron does not shift the half-wave potential of tungsten. Copper is precipitated as its oxalate, and thus does not interfere with tungsten determination. Vanadium gives a wave and completely distorts the tungsten polarogram, vanadium should therefore be absent in the solution of steel being polarographed.

We wish to thank S. S. Joshi for help in this work and for his advice, and also G. B. Singh for enabling this work to be carried out.

## SUMMARY

Reduction of sexivalent tungsten on a dropping-mercury cathode has been studied using oxalate as supporting electrolyte. A method has been developed for the successive determination of molybdenum and tungsten in a common supporting electrolyte. It has been shown that it is possible to determine iron and tungsten separately.

## LITERATURE CITED

[1] L. Meites, Analyt. Chem. 25, 1752 (1953); R. Pribil and A. Blazek, Collection Czechoslov. Chem. Commun. 16, 561 (1951).

[2] J. J. Lingane and I. A. Small, J. Am. Chem. Soc. 71, 973 (1949).

[3] I. M. Kolthoff and E. P. Parry, J. Am. Chem. Soc. 73, 6315 (1951).

[4] P. Souchay, Ann. Chim. 18, 61, 73, 169 (1943); 19, 102 (1944); 20, 73, 96 (1945); 21, 232 (1946).

[5] M. Von Stackelberg, P. Klinger, W. Koch, and E. Krath, Techn. Milt. Krupp Forsch. Schungsber. 2, 59 (1939).

[6] L. Meites, Polarographic Techniques (Interscience Publishers, Inc., New York, 1955) p. 289.

[7] L. E. Reichen, Analyt. Chem. 26, 1302 (1954).

[8] G. S. Deshmukh and J. P. Srivastava, Unpublished research.

[9] I. M. Kolthoff and J. J. Lingane, Polarography 2 (Interscience Publishers, Inc., New York, London, 1952) p. 477.

# AN EXTRACTION-PHOTOMETRIC DETERMINATION OF TRACES OF IRON BY MEANS OF 1-NITROSO-2-NAPHTHOL

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Of primary importance for scintillation materials is freedom from traces of iron which is a luminescence extinguisher [1]. In a search for highly sensitive and selective reactions for iron we settled on extraction of the intensely green-colored complex of $Fe^{2+}$ with 1-nitroso-2-naphthol, the absorption curve of which in isoamyl alcohol is shown in Fig. 1. This complex was described long ago by Il'inskii and Knorre [2]. Fischer [3] has indicated the possibility of an extraction-photometric determination of iron. Vanosi [4] has extracted the compound of divalent iron formed with ethyl acetate during detection of iron by a spot method. Kozo Sone [5] studied the compound of $Fe^{2+}$ and 1-nitroso-2-naphthol among a number of other anomalously colored inner-complex compounds of iron. While working with a solvent in which the complex is rapidly oxidized in the air, the author, however, established from spectrophotometric methods that its composition corresponds to a ratio of addendum to iron of 3:1.

Reagents, solutions, and measurement technique. A stock solution of ferric sulfate (1000 μg/ml) was prepared by oxidizing Mohr's salt (recrystallized chemically pure grade) in a sulfuric acid medium with hydrogen peroxide (medical). The concentration of the stock solution, from which the working solutions were prepared subsequently, was checked titrimetrically [6]. The solutions of the salts of the other metals were prepared from the recrystallized or chemically pure preparations. All the solutions of the metal salts were acidified with sulfuric (chemically pure) or nitric (redistilled from chemically pure acid) acid.

The organic solutions used were either chemically pure or analytical-grade materials; some of them were subjected to additional purification.

Ascorbic acid (medical, 10% solution) was dissolved in water saturated with $CO_2$, and stored in a darkened flask connected with a buret for measuring out the solution, and with a carbon dioxide source.

Solutions of 1-nitroso-2-naphthol were prepared by dissolving aliquots of the reagent in 120 ml of 1 N potassium hydroxide (chemically pure), and were purified from metals by shaking with chloroform, after which the solution was filtered and diluted with water to 1 liter.

Tartaric (analytical grade) and citric (chemically pure) acids, sodium hydrogen phosphate (recrystallized chemically pure), and sodium iodide (special purity), were used. Ammonia solutions were prepared by saturating water with gaseous ammonia. The water which was used was distilled twice in pyrex apparatus.

The extractions were carried out in separating funnels whose stopcocks were free from grease. The optical density was measured on a FÉK-M photoelectricolorimeter, and the pH on a LP-5 pH-meter fitted with a glass electrode. The absorption curves were taken on a SF-4 spectrophotometer. The results of all the measurements were treated statistically [7] at a confidence level of 0.95.

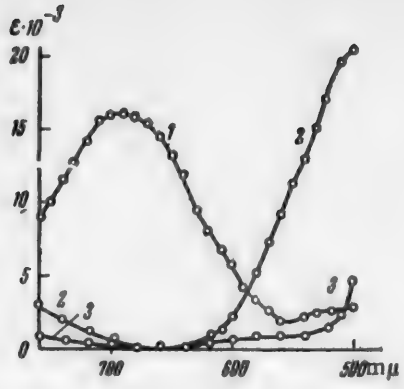


Fig. 1. Absorption curves of the compounds of divalent iron (1) cobalt (2), and nickel (3) with n-nitroso-2-naphthol in isoamyl alcohol. SF-4 spectrophotometer; concentrations of the solutions in isoamyl alcohol: 0.2, 2, and 2 μg of metal per ml,* respectively; cuvette with a layer thickness 10 mm.

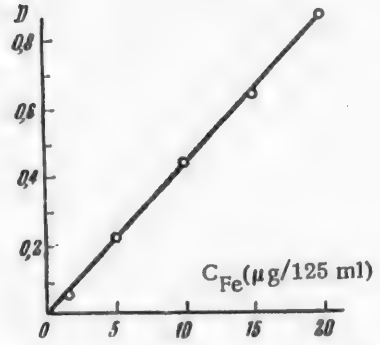


Fig. 2. Calibration curve for the determination of iron with 1-nitroso-2-naphthol.

Experimental conditions. $CCl_4$, $CHCl_3$, benzene, toluene, ethyl acetate, isoamyl acetate, and dichloroethane proved unsuitable for the extraction of the complex of $Fe^{2+}$ with 1-nitroso-2-naphthol on account of the flotation of the particles of the complex on the interface, and also because of the considerable weakening of the color of the extracts on standing. Isoamyl alcohol proved to be the best solvent.

In choosing a reducing agent we settled on ascorbic acid, although hydroxylamine hydrochloride can be recommended in certain cases. The latter permits determination in an acetate medium, but it is not completely suitable in the presence even of comparatively small amounts of tartrate or citrate ions. Ascorbic acid, as is evident from the results given below, permits determination to be carried out in the presence of large amounts of masking agents, which usually interfere with iron determination.

The optimum pH for reduction with ascorbic acid is 7.5 ± ± 0.5. This pH is readily established by neutralizing the aqueous solution of tartaric, citric, or phosphoric acids with ammonia using phenol red as indicator.

Construction of a calibration curve. Twenty ml of tartaric acid (0.05 M solution containing 15-20 drops of phenol red* ) was introduced into a separating funnel, this was followed by a measured volume of the standard ferric sulfate solution, and 5 ml of ascorbic acid. After the solution has been neutralized with ammonia to the phenol-red end point, 5 ml of the 1-nitroso-2-naphthol solution (0.2 g/liter) was added to the funnel, and, after 40 min, extraction was carried out with two lots of 10 ml of isoamyl alcohol. The combined extract was diluted with solvent to 25 ml in a standard flask and the optical density measured in a cuvette with a layer thickness of 5 cm using a red filter, measurements were made relative to the extract obtained in a control experiment (this extract differed from the working solution only in that the ferric sulfate solution was replaced by an equal volume of water, acidified in the same way as the working solution with sulfuric acid). Twenty-nine experiments carried out in order to get five points on the calibration curve showed that Beer's law is closely obeyed within the range 0.5-20 μg Fe. The slope of the calibration curve (optical density D – amount of Fe in μg) calculated by the method of least squares [7, 8] proved to be 0.4292 ± ± 0.00007; the deviation of the value of a free member from zero can be related to random causes (the straight line passes through the origin). The calibration curve is shown in Fig. 2.

Effect of foreign ions. Experiments with metallic ions were carried out by the same procedure as that adopted for constructing the calibration curve (a known amount of the salt of the respective metal was introduced into the working solution, as well as the iron salt). In experiments with masking agents, a measured volume of tartaric, or citric acid, or sodium monohydrogen phosphate, acidified with sulfuric acid was added to the separating funnel, this was followed by 15 ml of ascorbic acid solution, after the solution had been neutralized with ammonia, 5 ml of the 1-nitroso-2-naphthol solution (1 g/liter) was added and the solution diluted with water to 150 ml. The control experiment differed from the test experiment only in that the ferric salt solution was replaced by the corresponding volume of water acidified with sulfuric acid. The experimental results obtained are given in Table 1.

Since the nitroso-naphtholates of most metals, as well as the reagent itself, in contrast to ferrous naphtholate, do not have absorption bands in the red part of the spectrum, iron can be determined, as is evident

* A 0.1% solution in 20% ethanol.

TABLE 1

Determination of Iron in the Presence of Foreign Ions (5 μg $Fe^{3+}$ taken)

| Foreign ion X, mg | Ratio Fe : X* | No. of expt., n | Fe found, μg | Foreign ion X, mg | Ratio Fe : X* | No. of expt., n | Fe found, μg |
|---|---|---|---|---|---|---|---|
| $Ag^{+}$—0,05 | 1 : 10 | 3 | 5,13±0,48 | $Pb^{2+}$—5 | 1 : 1000 | 3 | 4,89±0,49 |
| $Al^{3+}$—5 | 1 : 1000 | 3 | 5,05±0,38 | $Tl^{+}$—5 | 1 : 1000 | 3 | 5,15±0,48 |
| $Cd^{2+}$—5 | 1 : 1000 | 3 | 4,96±0,59 | $UO_2^{2+}$—0,5 | 1 : 100 | 3 | 5,14±0,48 |
| $Co^{2+}$—0,02 | 1 : 4 | 5 | 5,34±0,49 | $Zn^{2+}$—5 | 1 : 1000 | 3 | 5,02±0,33 |
| $Cu^{2+}$—0,4 | 1 : 80 | 5 | 4,89±0,22 | $Zr^{IV}$—4 | 1 : 800 | 3 | 4,81±0,63 |
| $Ni^{2+}$—0,025 | 1 : 5 | 5 | 5,31±0,47 | $Cit^{3-}$—740 | $1 : 1{,}5 \cdot 10^5$ | 5 | 4,93±0,25 |
| $Mn^{2+}$—5 | 1 : 1000 | 3 | 5,19±0,59 | $PO_4^{3-}$—3580 | $1 : 7{,}2 \cdot 10^5$ | 5 | 4,96±0,27 |
| $MoO_4^{2-}$—0,5 | 1 : 100 | 3 | 5,14±0,44 | $Tart^{2-}$—4440 | $1 : 8{,}9 \cdot 10^5$ | 5 | 5,04±0,22 |

* In those cases where Fe : X > 1 : 1000, and also for $Cit^{3-}$, $PO_4^{3-}$, and $Tart^{2-}$, the ratios adduced in the test conditions are limiting values.

TABLE 2

Determination of Iron in Sodium Iodide (10 g of NaI and $Fe^{3+}$ were introduced into the test solution, and 10 g of NaI into the control)

| $Fe^{3+}$ introduced, μg | No. of determinations, n | Arithmethic mean for the values found μg (x̄) | Dispersion $S^2 \cdot 10^4$ | Accuracy, δ ± 0.95 | Error, % (relative) |
|---|---|---|---|---|---|
| 0,5 | 7 | 0,544 | 63,8 | 0,074 | 14,8 |
| 1 | 7 | 1,08 | 197,2 | 0,13 | 13,0 |
| 5 | 5 | 5,09 | 215,2 | 0,18 | 3,6 |
| 20 | 5 | 19,86 | 893,7 | 0,37 | 1,9 |

TABLE 3

Determination of Iron in Tartaric Acid (4.5 g of tartaric acid and $Fe^{3+}$ were added to the test solution, while only 4.5 g of tartaric acid was added to the control)

| $Fe^{3+}$ added, μg | No. of determinations, n | Arithmetic mean for the values found, $\bar{X}$ | Dispersion $S^2 \cdot 10^4$ | Accuracy $\pm \delta_{0.95}$ | Error, % (relative) |
|---|---|---|---|---|---|
| 1 | 7 | 1.04 | 239.5 | 0.14 | 14.0 |
| 5 | 5 | 5.04 | 325.2 | 0.22 | 4.4 |
| 10 | 5 | 9.94 | 272.5 | 0.21 | 2.1 |
| 20 | 5 | 19.87 | 649.7 | 0.32 | 1.6 |

from Table 1, even the presence of moderate amounts of $Co^{2+}$ and $Ni^{2+}$. The absorption curves of the respective naphtholates in isoamyl alcohol are shown in Fig. 1. $Cu^{2+}$ ions, apparently, are reduced under the given conditions and do not form a colored complex with 1-nitroso-2-naphthol; however, in the presence of large amounts of $Cu^{2+}$ the results for iron were low. Determination of iron cannot be carried out in the presence of large amounts of $Ag^{+}$, since this cation is reduced by the anion of ascorbic acid in an alkaline medium to the metal.

Determination of iron in "special purity" sodium iodide and in tartaric acid. Sodium iodide and other alkali metal halides used for producing scintillation monocrystals have to be highly pure. The methods suggested for determination of iron in this preparation [9, 10], however, are not sensitive enough ($1 \cdot 10^{-4} - 2.5 \cdot 10^{-5}$ %),

TABLE 4

Reproducibility of the Determination of Iron in Sodium Iodide and Tartaric Acid

| Preparation | No. of determinations, n | Arithmetic means for the values found (in μg Fe per g preparation) | Dispersion, $S^2 \cdot 10^4$ | Accuracy, $\pm \delta_{0.95}$ | Error, % (relative) |
|---|---|---|---|---|---|
| Sodium iodide "special purity" m = 10 g | 4 | 0.713 | 6.61 | 0.041 | 5.8 |
| Tartaric acid, analytical grade Δm = 4 g* | 5 | 1.73 | 19.47 | 0.055 | 3.2 |

* $\overline{m_1}$ = 4.5 g, $m_1$ = 0.5 g, $\Delta v_{NH_3}$ = 14.9 ml, q = $8.4 \cdot 10^{-3}$ μg, Fe in ml $NH_3$.

although a large amount of test material is used (20 g). The method suggested permits determination of down to $5 \cdot 10^{-6}$ % in a 10 g sample.

Experimental procedure. An aliquot of test material (up to 10 g) is placed in a 100 ml beaker and dissolved in 25 ml of ammonium tartrate solution (7.5 g of tartaric acid is dissolved in a small amount of water, 2-3 drops of phenol-red solution is added and the solution neutralized with ammonia; another 15-18 drops of the indicator solution is added and the whole diluted with water to 1 liter. Prior to use, 2 ml of a 3% solution of sodium thiosulfate is added per 100 ml of solution). The solution obtained is transferred to a 250 ml separating funnel. Into another separating funnel (control test) is added 25 ml of an ammonium tartrate solution. Next, to each of the funnels is added 15 ml of ascorbic acid and the solution immediately neutralized with ammonia using phenol red as indicator, 5 ml of 1-nitroso-2-naphthol solution (1 g/liter) is added and the solution diluted to approximately 150 ml with water and the whole mixed. After 40-50 min the solution is extracted twice with isoamyl alcohol, saturated beforehand with carbon dioxide (15, 10 ml), and the procedure adopted for constructing the calibration curve subsequently followed. In this case measurements should not be carried out later than one hour after commencing extraction.

Determination of iron in tartaric acid and its salts, as in other organic hydroxy acids, is carried out, as a rule, in the residue left after calcination [11]. This procedure is very long and contamination from metal vessels and from the air may occur. The method suggested permits determination of iron down to $1.25 \cdot 10^{-5}$ % without preliminary decomposition of the test preparation. In the procedure adopted use is made of a technique suggested earlier [12] for calculating the impurities in reagents during determination of traces in materials which are basic or acidic in character.

Experimental procedure. Two aliquots of tartaric acid differing in weight (e. g., 4.5 and 0.5 g) after dissolving in water, are transferred to 250 ml separating funnels. To each of the funnels is added 15 ml of ascorbic acid and a few drops of indicator, after neutralizing with ammonia, 5 ml of a solution of 1-nitroso-2-naphthol (1 g/liter) is added. The samples are then diluted with water to approximately 150 ml, the solutions are then thoroughly mixed, and after 40-50 min they are extracted twice with isoamyl alcohol (15, 10 ml). The procedure then followed is the same as that used for the construction of a calibration curve, and the first extract obtained from the large aliquot measured photometrically against the second. The iron content of 1 g of preparation (Z) is calculated by means of the formula:

$$Z = \frac{\Delta x - q(\Delta v)}{\Delta m},$$

where Δx is the iron content (in μg) corresponding to the optical-density reading, Δm is the difference in the two aliquots (in g), Δv is the difference in the volumes of ammonia used in neutralizing the two aliquots, and q is the iron content of 1 ml of ammonia established separately in a series of analyses (the measured volume of ammonia is evaporated in a beaker to dryness, the residue is dissolved in 20 ml of 0.05 M tartaric acid and the procedure used for constructing the calibration curve subsequently followed).

Results of checks on the methods of determining iron in the materials indicated are given in Tables 2 and 3.

In order to check on the reproducibility of the suggested methods, several determinations were made of iron in a sample of special-purity sodium iodide and in a sample of analytical-grade tartaric acid. The results are given in Table 4.

## SUMMARY

A study has been made of the conditions for using the reaction of $Fe^{2+}$ with 1-nitroso-2-naphthol for the extraction-photometric determination of traces of iron in highly pure materials.

The effect of a number of metal ions, as well as of citrate, tartrate, and phosphate ions on the reaction of iron with 1-nitroso-2-naphthol has been studied.

Methods have been developed for the determination of iron in sodium iodide for special purity and in tartaric acid, which permit determination of down to $5 \cdot 10^{-6}$ and $1.25 \cdot 10^{-5}$ % Fe, respectively.

## LITERATURE CITED

[1] A. V. Moskvin, Cathodoluminescence [in Russian] (Gostekhizdat, Moscow, 1949, Part 2) p. 107.

[2] M. Il'inskii and G. Knorre, Ber. 18, 2728 (1885).

[3] H. Fischer, Chem. Zentr. I, 2975 (1941).

[4] R. Vanossi, C. A. 35, 5412 (1941).

[5] Kozo Sone, Bull. Chem. Soc. Japan 25, I (1952).

[6] V. V. Ptitsyn and V. A. Kozlov, Zhur. Anal. Khim. 4, 35 (1949).

[7] N. P. Komar', Zhur. Anal. Khim. 7, 325 (1952).*

[8] W. J. Youden, Analyt. Chem. 19, 946 (1947).

[9] I. G. Shafran, Fifth Conference on Luminescence, Tartu, AN Éston.SSR 1957, p. 373.

[10] A. M. Bulgakova and A. K. Khukhryanskii, Trudy IREA, No. 23 (in the Press).

[11] Organic Reagents Coll. Standards [in Russian] (Standartgiz, Moscow, 1951) p. 234.

[12] A. B. Blank, Zhur. Anal. Khim. 15, 359 (1960).*

* Original Russian pagination. See C. B. Translation.

# SPECTROPHOTOMETRIC DETERMINATION OF TRACES OF NICKEL IN PURE INDIUM AND ALUMINUM

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Polarographic [1] or spectrographic [2, 3] methods are recommended for the determination of impurities in high-purity metals. Both methods require preliminary enrichment. Only one method is known which avoids the enrichment stage, this is the method by which nickel is determined in indium by means of dimethylglyoxime in the presence of an oxidizing agent. Unfortunately, this method has a low sensitivity and only permits determination of $2 \cdot 10^{-4}$ %; in addition, inference from copper is not excluded.

The aim of the work described here was to develop a method for determining nickel present as an impurity in the order of $10^{-6}$ %. The reagent used for nickel was α-furildioxime, which has a comparatively high sensitivity ($\epsilon$ = 19,000).

## EXPERIMENTAL

Reagents and apparatus. Because of the necessity of determining less than microgram amounts of nickel all the reagents used had to be purified.

Nitric and hydrochloric acids, as well as ammonia, were purified by distillation. A quartz retort was used for distilling the nitric acid, while apparatus made from molybdenum glass was used for distilling the hydrochloric acid and the ammonia. As tests showed, one distillation was sufficient. The reagents used which were chemically pure grade materials – sodium tetraborate, tartaric acid, and citric acid – were tested for the presence of nickel in them, under the same conditions as those used for the determination of nickel in the test materials. A solution of α-furildioxime in chloroform was used as the reference solution.

Nickel was not detected in the reagents used by means of the reaction with α-furildioxime ($D < 0.01$).

The standard nickel solution was prepared by dissolving nickel sulfate in water acidified with sulfuric acid. Solutions containing 1 μg nickel per ml were prepared by appropriate dilution on the day they were to be used. Chloroform was purified from alcohol and carbonyl chloride by washing with a 5% alkali solution followed by distillation. Maximum increase in sensitivity during measurement of the light absorption of a solution was achieved by decreasing its volume to 5 ml and by increasing the working length of the cell to 5 cm. In view of the small volume of liquid a limiter with a slit of 5 mm was used.

The optical density was measured on a SF-4 spectrophotometer.

Factors affecting the sensitivity of the reaction between nickel and α-furildioxime. The reaction between nickel and α-furildioxime has been studied in detail by a number of authors [4-6] as applied to the determination of more than 5 μg of nickel. It is recommended that the compound obtained be extracted by organic solvents (usually chloroform) at a pH of 7.3-8.3. In connection with the necessity of determining 0.05-0.5 μg of nickel, a study was made of the relation between completeness of extraction and pH over a wider acidity range. The

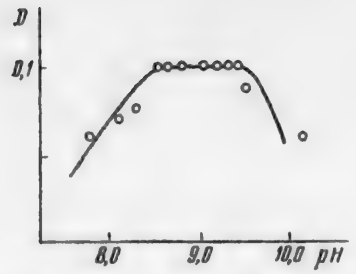


Fig. 1. Effect of the pH of the aqueous phase on the extractability of nickel.

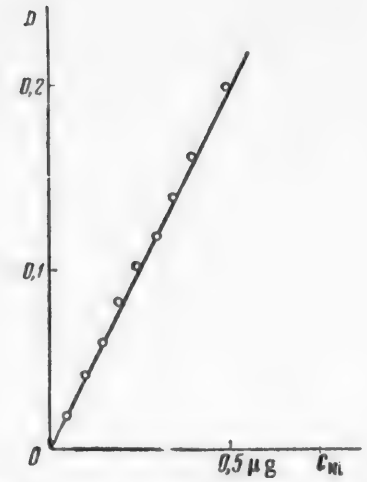


Fig. 2. Calibration curve for the determination of nickel with α-furildioxime; λ = 438 mμ; $l$ = 5 cm; V = = 5 ml.

results which are given in Fig. 1 indicated that completeness of extraction of 0.5 μg of nickel is achieved in a more alkaline region (pH 8.5-9.4).

In order to determine the value of the molar extinction coefficient, the complex nickel compound was isolated in the solid state; an aliquot of this material was then dissolved in chloroform. The molar extinction coefficient calculated from the light absorption of the chloroform solution proved to be 19,000 at 438 mμ.

In addition, it was established that during extraction of the complex compound with chloroform from a 25% aqueous-alcoholic solution, the molar extinction coefficient increases to 22,000. Acetone and dioxane exhibit the same effect. Chloroform solutions of nickel α-furildioximate conform to Beer's law down to 0.05 μg Ni in 5 ml (Fig. 2).

Effect of copper. Of the elements which accompany nickel, the one which has the greatest effect on its determination is copper, which forms with α-furildioxime a compound which is extracted by chloroform and also absorbs light at 438 mμ. It was found possible to eliminate interference on the part of copper by making use of differences in the stability of the ammines and α-furildioximates of copper and nickel. The complex compounds of copper and nickel were initially extracted with chloroform, the chloroform solutions were then washed with an ammonia solution 1:40. Results of these experiments are given in Table 1.

Determination of nickel in metallic indium and aluminum. Under the conditions used for determining nickel, indium and aluminum are precipitated as hydroxides. Accordingly tartaric and citric acids were added to the solutions; these acids do not affect the completeness of extraction of nickel α-furildioximate.

Determination of nickel in aluminum. One g of metallic aluminum is placed in a 100 ml quartz basin and dissolved in 10-15 ml of concentrated hydrochloric acid, the latter being added in small portions. The solution is evaporated almost to dryness and the residue transferred quantitatively by means of 30 ml of a 30% solution of sodium tartrate into a separating funnel, to which is then added 5 ml of a 0.1% solution of α-furildioxime and 25% alkali solution until the pH lies within the range 8.7-9.3 (checked by indicator paper).

After 2-3 min the complex compound which is formed is extracted twice with 2.5 ml lots of chloroform. The combined extracts are washed with 10 ml of ammonia (1:40). The volume of the chloroform solution of nickel α-furildioximate is then made up to 5 ml with chloroform and its optical density measured.

A solution of α-furildioxime in chloroform should be used as reference solution, this solution being obtained in the same way as the test solution. All the reagents used should be tested for any nickel present in them as impurity by the same method.

Results for the determination of nickel in aluminum in the presence and in the absence of copper are given in Tables 2 and 3. As is evident from these tables, nickel can be determined in metallic aluminum at a level of $5 \cdot 10^{-6}$% with a reproducibility of ± 20%; copper present in an amount which is one hundred times that of the nickel does not interfere.

TABLE 1

Determination of Ni in the Presence of Cu

| Ni introduced, μg | Ratio, Cu: Ni | Ni found, μg | Error, % |
|---|---|---|---|
| 0,50 | 10 : 1 | 0,49 | — 2,0 |
| 0,20 | 25 : 1 | 0,19 | — 5,0 |
| 0,10 | 50 : 1 | 0,11 | +10,0 |
| 0,05 | 100 : 1 | 0,05 | 0,0 |
| 0,05 | 100 : 1 | 0,05 | 0,0 |
| 0,05 | 100 : 1 | 0,045 | —10,0 |
| 0,05 | 100 : 1 | 0,06 | +20,0 |

Determination of nickel in metallic indium. One g of the metal is placed in a 100 ml quartz basin and dissolved in 10 ml of concentrated nitric acid. The solution is evaporated almost to dryness, and the dry residue transferred quantitatively into a separating funnel by means of 20 ml of a 20% tartaric acid solution. Five ml of a 0.1% solution of α-furildioxime is then added followed by 10 ml of concentrated ammonia. The pH of the solution is checked using indicator paper and some additional ammonia added until the pH lies within the range 8.7-9.3. After 2-3 min the complex compound obtained is extracted twice with 2.5 ml lots of chloroform. The combined extracts are washed with 10 ml of ammonia (1:40), and their volume adjusted to 5 ml with chloroform, the optical density is then measured as indicated above. During the extraction process a small amount of the precipitate of the double tartrate of indium and ammonium is formed; this precipitate, however, does not affect the results of the determination of nickel.

TABLE 2

Determination of Nickel in Metallic Aluminum (1 g sample)

| Ni introduced | | Ni found, μg | Error, % | Ni introduced | | Ni found, μg | Error, % |
|---|---|---|---|---|---|---|---|
| μg | % | | | μg | % | | |
| 0,50 | $5\cdot10^{-5}$ | 0,51 | +2,0 | 0,30 | $3\cdot10^{-5}$ | 0,28 | —5,6 |
| 0,50 | $5\cdot10^{-5}$ | 0,49 | —2,0 | 0,10 | $1\cdot10^{-5}$ | 0,12 | +5,0 |
| 0,50 | $5\cdot10^{-5}$ | 0,52 | +4,0 | 0,05 | $5\cdot10^{-6}$ | 0,05 | 0,0 |
| 0,30 | $3\cdot10^{-5}$ | 0,29 | —3,3 | 0,05 | $5\cdot10^{-6}$ | 0,06 | +20,0 |
| 0,30 | $3\cdot10^{-5}$ | 0,30 | 0,0 | 0,05 | $5\cdot10^{-6}$ | 0,04 | —20,0 |

TABLE 3

Determination of Nickel in Metallic Aluminum in the Presence of Copper ( 1 g sample)

| Ni introduced μg | Ratio Ni: Cu | Ni found | | Error, % | Ni introduced μg | Ratio Ni: Cu | Ni found | | Error, % |
|---|---|---|---|---|---|---|---|---|---|
| | | μg | % | | | | μg | % | |
| 0,50 | 1 : 10 | 0,52 | $5\cdot10^{-5}$ | +4,0 | 0,10 | 1 : 50 | 0,08 | $1\cdot10^{-5}$ | —20,0 |
| 0,40 | 1 : 12,5 | 0,42 | $4\cdot10^{-5}$ | +5,0 | 0,05 | 1 : 100 | 0,04 | $5\cdot10^{-6}$ | —20,0 |
| 0,30 | 1 : 16 | 0,29 | $3\cdot10^{-5}$ | —3,3 | 0,05 | 1 : 100 | 0,06 | $5\cdot10^{-6}$ | +20,0 |
| 0,20 | 1 : 25 | 0,23 | $2\cdot10^{-5}$ | +10,5 | | | | | |

TABLE 4

Determination of Traces of Nickel in Metallic Indium (1 g sample)

| Ni introduced | | Ni found, μg | Error, % | Ni introduced | | Ni found, μg | Error, % |
|---|---|---|---|---|---|---|---|
| μg | % | | | μg | % | | |
| 0,05 | $5\cdot10^{-6}$ | 0,055 | +10,0 | 0,05 | $5\cdot10^{-6}$ | 0,040 | —20,0 |
| 0,05 | $5\cdot10^{-6}$ | 0,045 | —10,0 | 0,05 | $5\cdot10^{-6}$ | 0,050 | 0,0 |
| 0,05 | $5\cdot10^{-6}$ | 0,045 | —10,0 | 0,05 | $5\cdot10^{-6}$ | 0,065 | +25,0 |
| 0,05 | $5\cdot10^{-6}$ | 0,050 | 0,0 | 0,10 | $1\cdot10^{-5}$ | 0,110 | +10,0 |
| 0,05 | $5\cdot10^{-6}$ | 0,050 | 0,0 | 0,15 | $1,5\cdot10^{-5}$ | 0,135 | —10,0 |
| 0,05 | $5\cdot10^{-6}$ | 0,060 | +20,0 | | | | |

TABLE 5

Determination of Nickel in Indium in the Presence of Copper (0.5 g sample)

| Ni introduced, μg | Ratio Ni:Cu | Ni found | | Error, % | Ni introduced, μg | Ratio Ni:Cu | Ni found | | Error, % |
|---|---|---|---|---|---|---|---|---|---|
| | | μg | % | | | | μg | % | |
| 0,50 | 1 : 10 | 0,49 | $1 \cdot 10^{-4}$ | —2,0 | 0,15 | 1 : 33 | 0,14 | $3 \cdot 10^{-5}$ | —6,6 |
| 0,25 | 1 : 20 | 0,21 | $5 \cdot 10^{-5}$ | +4,0 | 0,10 | 1 : 50 | 0,11 | $2 \cdot 10^{-5}$ | +11,0 |
| 0,20 | 1 : 25 | 0,18 | $4 \cdot 10^{-5}$ | —10,0 | 0,05 | 1 : 100 | 0,06 | $1 \cdot 10^{-5}$ | —20,0 |

Tables 4 and 5 contain results obtained during the determination of nickel in metallic indium in the presence and in the absence of copper. It follows from the results given in these tables that nickel can be determined in metallic indium at a level of $5 \cdot 10^{-6}$% with a reproducibility of ±25%; copper present in an amount one hundred times that of nickel does not interfere with the determination.

## SUMMARY

Conditions have been established for the spectrophotometric determination of small amounts of nickel — down to 0.05 μg — by means of α-furildioxime, in solutions of its pure salts and also in the presence of one hundred times its amount of copper, by using an extraction method.

A method has been developed for determining traces of nickel in metallic aluminum at a level of $5 \cdot 10^{-6}$% with a reproducibility of ± 20%, and in metallic indium at a level of $5 \cdot 10^{-6}$% with a reproducibility of ±25%.

## LITERATURE CITED

[1] F. Pohl and W. Z. Ronsels, Analyt. Chem. 161, 108 (1958).

[2] F. Pohl, Z. Anal. Chem. 142, 19 (1954).

[3] O. Koch, Mikrochim. acta N 1, 92 (1958).

[4] V. M. Peshkova, G. A. Goncharova, E. A. Gribova, and I. V. Puzdrenkova, Zhur. Anal. Khim. 8, 114 (1953).*

[5] A. Gahler, A. Mitchell, and M. Mellon, Anal. Chem. 23, 500 (1951).

[6] G. Taylor, Analyst 81, 369 (1956).

* Original Russian pagination. See C. B. Translation.

# DETERMINATION OF MICROCONTENTS OF SELENIUM IN ORES AND ROCKS

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In connection with the development of geochemical methods of prospecting for scattered ore deposits, the necessity has arisen of determining selenium not only in ores but also in enclosing rocks with a sensitivity of the order of $8 \cdot 10^{-5}$ %. Current methods of determining small amounts of selenium in sulfide ores are based on measuring the optical density of elemental selenium sols [1, 2], and are applicable for selenium contents in the test rocks ranging from 0.001% upwards. The difficulty in developing a more sensitive method consists primarily in choosing a method for decomposing the samples. Current methods of decomposition, and of removing $HNO_3$ on heating acid solutions [1-6] cannot be used, since, at low selenium contents, even small losses of this element, because of its volatility, have a pronounced effect on the experimental results. For microgram amounts of selenium these losses can amount to 100% even in the absence of chlorides.

Very serious difficulties are also met during separation of microgram amounts of selenium. High sensitivity of the photometric finish itself is also desirable.

We have developed a method for the determination of selenium in ores and rocks which has a sensitivity of $10^{-4}$ %; it is based on the acid-oxidation decomposition of test material, separation of selenium with ferric hydroxide and a photometric finish.

The individual stages of the technique as applied to microgram amounts of selenium were studied as a preliminary; these included: reduction and photometric determination, concentration by coprecipitation with ferric hydroxide, and decomposition of test material.

Reduction and photometric determination. Ascorbic acid was used for reducing selenium to the elemental state. Reduction was effected in a hydrochloric acid medium in tubes which can be centrifuged.

In order to concentrate and separate the reduced colloidal selenium from solution, coprecipitation and centrifuging with barium sulfate was used. For this purpose, ammonium sulfate and a known amount of barium chloride solution were added to a colloidal solution of selenium contained in a tube. The $BaSO_4$ formed entrained the elemental selenium, and, after centrifuging, a precipitate of barium sulfate colored rose by the selenium settled out on the bottom of the tube. As our tests showed, it is sufficient to add 150-200 mg of $(NH_4)_2SO_4$ and 1 ml of a 10% solution of $BaCl_2$ to 10 ml of a colloidal selenium solution. Under such conditions selenium passed completely into the $BaSO_4$ precipitate. The color intensity of the precipitate is reproducible and is proportional to the selenium content of the solution. On this basis it proved possible to prepare a scale of standards for determining selenium. It is most convenient to use as a standard scale $BaSO_4$ precipitates containing 0, 10, 15, 20, and 30 μg of Se. At higher selenium contents the gradation in the color intensity is not sufficiently marked. The smallest amount of selenium which is clearly discernible is 2 μg.

TABLE 1

| HCl concentration, N | Se taken, μg | Se found, μg |
|---|---|---|
| 0,1 | 15 | 10 |
| 1,0 | 15 | 13 |
| 4,0 | 15 | 15 |
| 10,0 | 15 | 10 |

TABLE 2

| Duration of reduction, min | Se taken, μg | Se found, μg |
|---|---|---|
| 2 | 15 | 8 |
| 6 | 15 | 12 |
| 10 | 15 | 13 |
| 45 | 15 | 15 |

TABLE 3

| Time after acidification, min | Se taken, μg | Se found, μg |
|---|---|---|
| 3 | 15 | 7,5 |
| 6 | 15 | 9 |
| 11 | 15 | 11 |
| 20 | 15 | 12,5 |
| 40 | 15 | 15 |
| 60 | 15 | 15 |

Such an experimental technique, in the first case, is more sensitive than the method of observing the colors through the thickness of a solution because the selenium is concentrated in a small (about 0.1 g) compact precipitate. Secondly, the color of the test solution, in the given instance, does not interfere, since the color of the precipitate is observed through the bottom of the tube. Thirdly, an important advantage of this method is the fact that such a standard scale is stable for a long time, at least for several months.

Selenious acid is reduced by ascorbic acid in both hydrochloric and sulfuric acid solutions. In the cold, however, reduction proceeds very slowly. Heating hydrochloric and, particularly, sulfuric acid solutions of ascorbic acid leads to rapid decomposition of the latter. On the basis of a number of experiments it was found that maximum reduction occurs when the ascorbic acid is introduced into a hydrochloric acid solution of selenious acid heated beforehand to 60-80°.

In order to evaluate the results of a study on the effect of acidity on the efficiency of reduction, and on the time necessary for complete reduction of selenious acid, a standard scale was prepared as described above. Reduction was carried out in hot solutions in a medium of 4 N hydrochloric acid. Barium sulfate was precipitated one hour after addition of ascorbic acid. In Table 1 is shown the extent of reduction of selenium 30 min after addition of ascorbic acid, as a function of the hydrochloric acid content of the solution. In Table 2 are given results which show the degree of reduction of selenious acid in 4 N HCl as a function of time. These results are reproducible to an accuracy of ± 1 μg. As is evident from Tables 1 and 2, the optimum hydrochloric acid concentration for reducing selenium is 4 N. In such a solution selenium is completely reduced in 20-30 min. The drop in reduction efficiency in 10 N HCl is explained by the instability of ascorbic acid in strongly acid solutions; it is also possible that selenium is lost on heating. As experiments showed, under such conditions, quantitative reduction of tellurium also occurs in a hydrochloric acid medium; tellurium, like selenium, passes into the barium sulfate precipitate and interferes with determination of selenium. In addition, gold present in solution, which usually leads to complications during the photometric determination of selenium [1], is also reduced with selenium.

In order to remove selenium from tellurium and other possible impurities, we made use of the capacity of selenium to dissolve in a concentrated solution of sodium sulfite to form selenosulfate [7, 8], which is destroyed on acidification to liberate elemental selenium. In order to dissolve the selenium from the $BaSO_4$ precipitate it is sufficient to heat it on a water bath for 5-10 min with 10% $Na_2SO_3$ which is 0.25 M with respect to $Na_2CO_3$.

Decomposition of the selenosulfate to yield elemental selenium on acidifying the solution does not occur instantaneously, but requires a definite time. In order to establish the time required for complete liberation of selenium, an equal volume of concentrated hydrochloric acid was added to its sulfite solution, and, after the turbulent liberation of $SO_2$ had ceased, the tube plus solution was placed in hot water. After a definite time the barium sulfate was precipitated and centrifuged as described above.

It is clear from Table 3 that complete liberation of selenium from its sulfite solution is only achieved 40 min after addition of acid. The colloidal selenium isolated in this way, free from foreign impurities, can be centrifuged again with a $BaSO_4$ precipitate.

Concentration by coprecipitation with ferric hydroxide. As a basis of the method a technique suggested by Proshkovich and Faleev [6] was used, their technique is based on coprecipitation of selenious acid with ferric

TABLE 4

| Test material | Weight of aliquot, g | Se determined in the aliquot, μg | Se added, μg | Total Se, μg | Se determined in the sample, % |
|---|---|---|---|---|---|
| Breccia rock 1 | 0.25 | 16 | 10 | 27 | $6.4 \cdot 10^{-3}$ |
| " " 2 | 2.0 | 28 | | | $1.4 \cdot 10^{-3}$ |
| Mineralized serpentite | 5.0 | 4 | 10 | 14 | $0.8 \cdot 10^{-4}$ |
| Phyllite with pyrrhotine minerals | 2.0 | 11 | | | $5.5 \cdot 10^{-4}$ |
| Phyllite with quartz-carbonate streaks | 2.0 | 3 | | | $1.5 \cdot 10^{-4}$ |

hydroxide at a pH of 5.2, which is achieved by means of zinc oxide. At this pH complete coprecipitation of selenium occurs. Under such conditions nickel and a large fraction of copper remain in solution. At the same time selenium is separated from nitrate ions. Experiments carried out with solutions of selenious acid showed that for iron contents of the solution ranging from 50 to 500 mg, coprecipitation is complete. The volume of the test solution (from 50 to 300 ml), and any alkali metal salts present in solution in amounts up to 0.1 g/ml have no effect on completeness of coprecipitation.

Decomposition of test material. In view of unavoidable losses of selenium on heating acid solutions, we examined the possibility of decomposing samples of test material by prolonged action of aqua regia in the cold.

The test material used was various sulfide ores and rocks containing different amounts of sulfide. From 0.2 to 5 g of the finely ground sample was covered with aqua regia and allowed to stand overnight. The selenium content of the solution obtained was then determined. In order to check on completeness of decomposition, the undissolved residue was again subjected to the prolonged (16-18 hours) action of aqua regia. No selenium was found in the solution obtained after the second treatment in any one of the eight experiments carried out.

Experimental procedure. From 0.5-5.0 g of finely ground test material was placed in a conical flask and moistened with water, 25 ml of aqua regia was then added and the whole left to stand overnight. The undissolved material was filtered off through a No. 4 glass crucible. The solution was diluted with water to 150-200 ml, and 100-200 mg of ferric iron in the form of a solution added (when the amount of iron already in the solution is not enough), the solution was neutralized, first with an alkali solution, and then with an aqueous suspension of zinc oxide, and the whole heated on a water bath until the precipitate had coagulated completely. The supernatant liquid was decanted. The ferric hydroxide precipitate was washed by decantation until the wash liquors gave a negative test for nitrate ions. The wash liquor was prepared by neutralizing 0.05-0.1 N $H_2SO_4$ with zinc oxide. The washed precipitate was transferred to a tube and centrifuged, after which it was dissolved in the minimum amount of concentrated HCl, 3.5-4 ml of the latter was added in excess, and the volume made up to 10 ml with water. Tube plus solution were heated on a water bath to 70-80°, dry ascorbic acid was then added until the iron was completely reduced, when a further 300-500 mg of ascorbic acid was added in excess. After 30-40 min, 150-200 mg of $(NH_4)_2SO_4$ and 1 ml of a 10% $BaCl_2$ solution were added to the solution. The whole was centrifuged. The precipitate was washed first with hydrochloric acid 1:1, and then with water. To the washed precipitate was added 2 ml of a 10% $Na_2SO_3$ solution containing 0.25 g-mole/liter of $Na_2CO_3$ and the mixture heated on a water bath for 10 min. After centrifuging, the solution was transferred to another tube. This operation was repeated twice. To the sulfite solution (or an aliquot of this solution) was added an equal volume of concentrated HCl and the tube placed in hot water. After 40-50 min a second precipitation was carried out and the $BaSO_4$ centrifuged. From the intensity of the rose color of the precipitate on the bottom of the tube, using the standard scale the selenium content was determined.

In order to prepare a standard scale, appropriate amounts of selenious acid were added to solutions containing 25 ml of aqua regia and 200-300 mg of ferric iron. The solutions were neutralized and ferric hydroxide precipitated; the procedure subsequently followed was the same as that described above.

In order to check that selenium is not lost during the decomposition stage and during the subsequent analytical procedure, experiments were carried out in which known amounts of a selenious acid solution were added to aliquots of test material. Results for the determination of selenium in several ores and rocks are given in Table 4.

As indicated above, the smallest amount of selenium which can be determined is 2 μg, which for an aliquot material of several grams is equivalent to a sensitivity of the order of $10^{-4}$%. The size of the aliquot is limted by the iron content of the sample. When the iron content of the aliquot exceeds 500-600 mg, the operations of separating the hydroxide precipitate from the solution and further reduction are complicated.

The accuracy for the determination of selenium when the amount of the latter in an aliquot is less than ten micrograms is 20-30%; for higher selenium contents the error is of the order of 10%.

## SUMMARY

A study has been made of the conditions for reducing microgram amounts of selenium by ascorbic acid in hydrochloric acid solutions.

A new method has been developed for the determination of selenium; it is based on coprecipitation and centrifuging of elemental selenium with barium sulfate, and comparing the color intensity of the precipitate obtained with standards.

For the determination of microamounts of selenium a method of decomposing ores and rocks with aqua regia in the cold is suggested.

The method developed permits determination of selenium in ores and rocks with a sensitivity of the order of $10^{-4}$ %.

## LITERATURE CITED

[1] S. T. Volkov, Zavodskaya Lab. 5, 1429 (1936); Determination of Selenium and Tellurium in Ores and Concentrates Containing Gold, Gosgeolizdat, Moscow-Leningrad, 1945.

[2] V. K. Zemel', Zavodskaya Lab. 5, 1438 (1936).

[3] M. V. Markova, A Method for the Determination of Selenium and Tellurium in Ores and Their Processed Products, Information Center of the Ministry of Nonferrous Metallurgy, USSR, Information No. 194, 1956.

[4] S. Yu. Fainberg, Analysis of Nonferrous Ores [in Russian] (Metallurgizdat, Moscow, 1953) p. 542.

[5] Analysis of Mineral Raw Material, Edited by Yu. N. Knipovich and Yu. V. Morachevskii [in Russian] (Goskhimizdat, 1956) p. 841.

[6] M. F. Proshkovich and P. V. Faleev, Obogashchenie Rud. No. 2, 21 (1957).

[7] B. V. Nekrasov, Course in General Chemistry [in Russian] (Goskhimizdat, Moscow, 1952) p. 319.

[8] V. F. Toropova, Zhur. Anal. Khim. 11, 599 (1956).*

* Original Russian pagination. See C. B. translation.

# DETERMINATION OF FLUORINE IN METALLIC ZIRCONIUM BY MEANS OF A DISCHARGE IN A HOLLOW CATHODE

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A study carried out earlier on discharges in a hollow cathode under high temperature conditions [1], has enabled the reactions which occur to be used for the spectrographic determination of small amounts of fluorine in metallic zirconium. Methods have been published on the spectrographic determination of fluorine and other halogens in difficultly volatile samples, mainly oxides, using as a light source a discharge in a hollow cathode in a helium atmosphere [2-4]. Fluorine is determined on the basis of atomic "quasiresonance" lines lying in the red and near-infrared parts of the spectrum. The sensitivity of the method is $1 \cdot 10^{-4}$% for an accuracy of ±10-15%.

Experiments which we have carried out in order to establish the possibility of using a similar method for the determination of fluorine in metallic zirconium have shown that the sensitivity obtained in this case is low (about 0.01%). The following are probably the reasons for this low sensitivity. Firstly, it is quite possible that the atomic lines of fluorine which are difficult to excite are weakened (the excitation potential of the corresponding energy levels is about 15 ev), when an appreciable amount of the main element of the sample – zirconium – passes into the discharge zone, since the ionization potential of the ions of this element is comparatively low – 6.95 ev. Although at a current intensity of about 300 ma, the source temperature (about 1000°) is still not high enough for appreciable evaporation of the zirconium (the vapor pressure at 1500° is about $1 \cdot 10^{-5}$ mm Hg [5]), the discharge spectrum nevertheless contains fairly intense zirconium lines, presumably as a result of sputtering of the test material on the cathode. At high current densities evaporation of zirconium becomes an essential factor (the vapor pressure is 0.01 mm Hg at 2000° and is 0.1 mm at 2200°). Secondly, the low intensity of the atomic lines of fluorine may be determined by the occurrence of secondary reactions. It is known that fluorine, like the other halogens, readily reacts on heating with zirconium [6], the very stable zirconium fluoride being formed (heat of formation 445 kcal). If it is assumed that the fluorine contained in the zirconium participates in the discharge mainly in the form of its compound with zirconium, the low sensitivity of an analysis based on the atomic lines becomes quite understandable. But, in such a case, it should be possible to develop a satisfactory method for determining fluorine by using the molecular spectrum of the compound which is most stable under the discharge conditions. Such a technique has been successfully used for the determination of fluorine [7-11]. The fluorine contained in test material is converted into its compound with calcium, strontium or silicon, and the determination is carried out on the basis of the molecular band of CaF or SrF, or on the basis of the atomic lines of silicon.

We detected in the spectra of samples of metallic zirconium obtained by the electrolysis of fused fluoride salts of zirconium an intense molecular band with a violet tinge.* The wavelength of the edge of the band was 2274.5 A. A microphotogram of it is shown in Fig. 1. We were unable to find any published information on this band or its nature. Accordingly, a series of special experiments were carried out which enabled us to establish

* We detected in the region 2300-2350 A two further molecular bands which presumably form, together with the band noted, a system of bands.

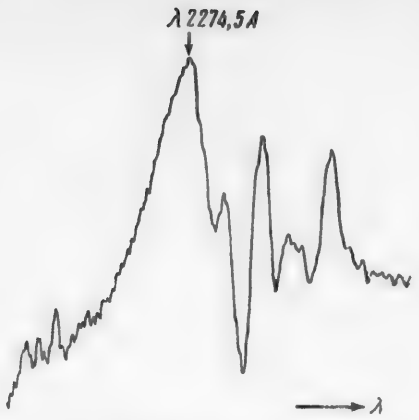


Fig. 1. Microphotogram of the band with an edge at λ 2274.5 A.

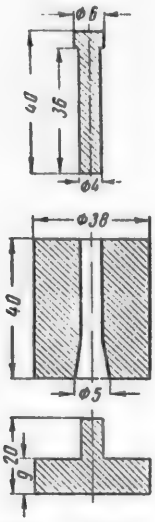


Fig. 2. Press form.

that the band detected actually belongs to a compound of fluorine with zirconium, its concentration being proportional to the fluorine concentration of the zirconium sample. We were unable to establish to which particular zirconium compound this molecular band belongs.

It was established that the band with an edge at λ 2274.5 A is present in the spectrum of a discharge in a hollow cathode in a helium atmosphere, both when graphite and metallic cathodes were used. The band indicated is also excited when zirconium dioxide containing fluorine in the form of $TaF_5$, NaF, or $CaF_2$ is placed in the cathode. The use of this band permits the determination of fluorine in zirconium dioxide with a sensitivity of $1 \cdot 10^{-3}$%.

Preparation of zirconium samples containing known amounts of fluorine presents some difficulties. There are no reliable chemical methods for determining fluorine in metallic zirconium. It might be assumed that fluorine is contained in the metal in the form of potassium fluorozirconate, potassium fluoride, or zirconium fluoride. It is also possible that fluorine may be present as a compound with other elements found in metallic zirconium, but the probability of this being the case is low. Accordingly, in order to prepare standard samples, potassium fluorozirconate or KF was added to filings of zirconium iodide, in whose spectrum the band with an edge at λ 2274.5 A was absent. The filings were obtained by filing compact zirconium with a clean file. The filings were then sieved through a No. 0315 sieve demagnetized and washed with hydrochloric acid, distilled water, and alcohol. The mixture was ground in a tantalum mortar for 1.5 hours.

Filings of the test samples were prepared in the same way (without the grinding operation). In order to increase the reliability of the determination, aliquots of the standard samples and of the test samples were converted into brickettes by means of a press form (Fig. 2) and a laboratory hydraulic press at a pressure of 15 tons/cm$^2$.

The setup described previously [1] with a hollow cathode was used for exciting the spectra of the test samples. The atomic lines of fluorine (6856.0 A and 7128.0 A) and the molecular band with an edge at λ 2274.5 A were photographed at the same time on an ISP-51 spectrograph (with a UF-84 camera) and on an ISP-22 spectrograph. Photographic plates type "Infra-720" or "Paninfta" were used with the first apparatus, and "Spectrographic type III" or "Micro" were used in the second.

In experiments with brickettes of standard samples and test samples of electrolytic zirconium, the following facts were established:

1. The change in blackening of the edge λ 2274.5 A and of the atomic lines of fluorine with time is the same, for all the values of the discharge current tested (from 300 to 1200 ma). This holds true for both the standards and for the metal samples.

2. The intensity of the molecular band and of the atomic lines increases with increasing current intensity.

3. Conditions for determination on the basis of the edge at λ 2274.5 A are more favorable than those obtaining for the atomic lines of fluorine, since in the 7000 A region there is a strong continuous background

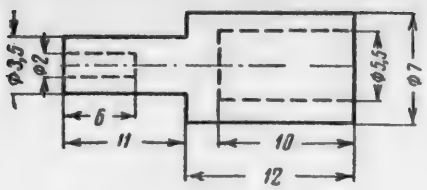


Fig. 3. Graphite cathode.

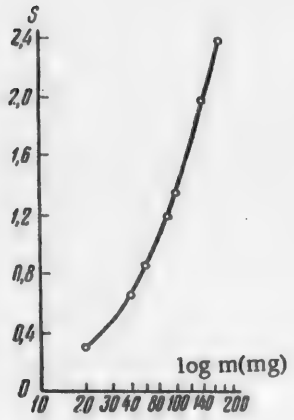


Fig. 4. The relation between the blackening of the band edge at λ 2274.5 A and the weight of the sample.

from the calcined sample on the cathode, while there is no background in the 2300 A region.

The sensitivity of the determination of fluorine based on the atomic lines is much lower than the sensitivity of determination based on the edge at λ 2274.5 A, and, as already mentioned, amounts to about $1 \cdot 10^{-2}$ %.

4. The most reproducible results, at a maximum intensity of the band edge at λ 2274.5 A, are obtained when the brickette is fused in a graphite cathode. The current intensity necessary for this depends (for constant cathode dimensions) on the size of sample, and also on the position of the brickette in the cathode. In accordance with data [12] on the increase in the intensity of ionic bombardment when the field in the cathode is not homogeneous, it was established that when the brickette lies on the lateral surface of the cathode, it melts at the lowest intensity of the discharge current. When a 50 mg sample is used in a cathode with the dimensions shown in Fig. 3, the brickette melts at a current intensity of 1000-1100 ma. In this case the fluorine is "burnt out" completely (according to the edge at λ 2274.5 A) in 60-90 sec for samples with a fluorine content of 0.1%.

5. Simultaneous recording of the potassium resonance lines λ 7664.9 and λ 7699.0 A on an ISP-51 spectrograph and of the edge at λ 2274.5 A made it possible to establish that for a sample of the original (not remelted) electrolytic zirconium, the blackening of the potassium line changes in accordance with the blackening of the band edge at λ 2274.5 A. This indicates that in the original zirconium, fluorine is present mainly as potassium fluorozirconate and KF.

In the case of remelted electrolytic zirconium this correspondence is not observed, and it is most probable that in such samples fluorine is present in the form of zirconium fluoride; this is also confirmed by a comparison of the corresponding thermodynamic constants [13].

6. The blackening of the band edge at 2274.5 A and the nature of these changes with time as a function of the helium pressure in the discharge tube change insignificantly within the pressure range studied (6-15 mm Hg).

7. The blackening of the edge at λ 2274.5 A strongly depends on the weight of sample (Fig. 4).

8. The sensitivity of the determination of fluorine based on the molecular band at λ 2274.5 A is $3 \cdot 10^{-4}$, for a sample weight of 50 mg. The sensitivity can be readily increased to $3\text{-}5 \cdot 10^{-5}$% by increasing the sample weight to 80-120 mg.

9. The optimum working conditions for determination of fluorine in the concentration range $3 \cdot 10^{-4} - 1 \cdot 10^{-2}$ % are as follows: sample weight, 50 mg; discharge current, 1100 ma; exposure, 60-90 sec; helium pressure, 8 mm Hg; photographic plates, "Spectrographic Type III" or "Micro"; slit width of the ISP-22 spectrograph, 30-35 μ. The working curve is constructed within the coordinates S, log C.

In order to be sure of the absence of systematic errors arising from variations in the behavior of fluorine in synthetic samples and in samples of metal, and as a result of third-component effects, we made a comparison of changes with time of the blackening of the analytical band with an edge at 2274.5 A for brickettes of synthetic mixtures containing fluorine in the form of potassium fluorozirconate and in the form of $CaF_2$, and for samples of electrolytic zirconium. The nature of the changes in blackening with time proved to be very close for all samples at a current intensity of 1100 ma (when the brickette was fused), while at lower current intensities, when the brickettes were not molten, appreciable differences were observed (Fig. 5).

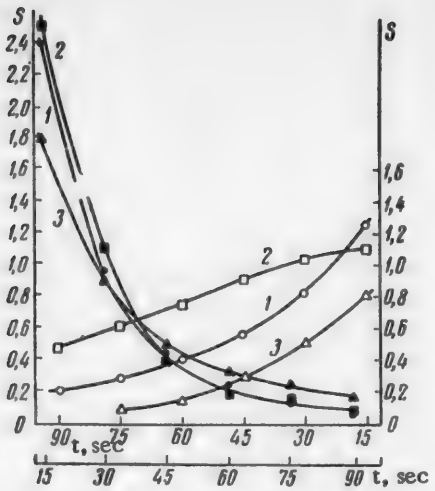


Fig. 5. Change of blackening of the edge at λ 2274.5 A with time. 1) Zr standard + $K_2ZrF_6$ (0.03% F); 2) Zr standard + $CaF_2$ (0.03% F); 3) sample of electrolytic zirconium Zr; Δ, □ – i = = 500 ma (the sample did not fuse); ●, ▲, ■ – i = 1100 ma (the sample fused).

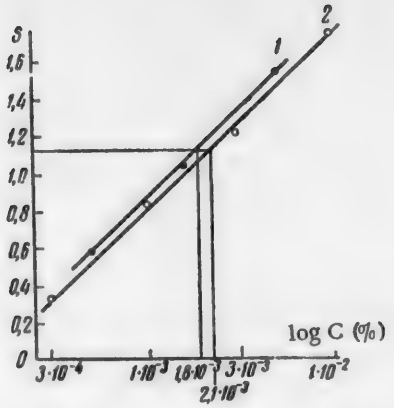


Fig. 6. Working curves for the determination of fluorine in zirconium. 1) Fluorine introduced as $CaF_2$; 2) fluorine introduced as $K_2ZrF_6$.

Two working curves were constructed for two series of standard samples, in one of which fluorine was introduced as potassium fluorozirconate, while in the other it was introduced as $CaF_2$. As is evident from Fig. 6, these curves have equal slopes and only suffer from a slight parallel displacement. Results obtained for synthetic mixtures of zirconium iodide with potassium fluorozirconate ($2 \cdot 10^{-3}$ % fluorine), by both working curves, coincide within the limits of the error of the method (see below). This fact enables one to make some conclusions on the role of tertiary components during the determination of fluorine on the basis of the edge of the molecular band at 2274.5 A. When fluorine is introduced in the form of potassium fluorozirconate, the standard mixtures contain graduated concentrations of potassium (approximately 1:1.5 relative to the fluorine content, in accordance with the stoichiometric ratio). When, under such conditions, the working curves almost coincide with curves constructed on the basis of standards not containing elements with low ionization potentials (standards with $CaF_2$), this indicates the absence of the effect of such elements on the intensity of the analytical band for contents of the third elements of about 0.01%. In order to establish how higher concentrations of elements with low ionization potentials affect the determination, a comparison was made of the analytical results obtained for fluorine for samples of electrolytic zirconium with the results for the same samples to which had been added 0.1% sodium as NaCl (Table 1). The original Na content of the sample was 0.01%, K << 0.01%.

Thus, when the sample contains high contents of the alkali metals, there is a danger that there will be an appreciable decrease in the results for the determination of fluorine, if measures are not taken to bring the composition of the standards close to that of the samples. This danger is, however, not so great when it is remembered that the alkali metal content does not exceed a few hundredths part of a percent.

Experiments with standards prepared by introducing fluorine in the form of $CaF_2$, which has been comparatively well studied, were useful from the point of view that they made it possible to make some conclusions regarding the behavior of fluorine during the analytical process as a function of the nature of the compound in which it is present in the sample. It is known that $CaF_2$ is a very stable compound (heat of formation 290.3 kcal [13]). When it is introduced into the light source molecular bands of CaF appear in the spectrum. Under the conditions which we used, however, the molecular bands of this compound were not present in the spectrograms of the series of standards to which $CaF_2$ had been added. It could be concluded from this that the side chemical reactions of fluorine with impurity elements present in the zirconium should not appreciably affect the results of fluorine determination. The results should not be distorted even in the case when fluorine is present in the zirconium in the form of compounds with impurity elements, as long as the stability of these compounds is not appreciably higher than that of $CaF_2$.

TABLE 1

| Sample | No. 1 | No. 1 + + 0.1% Na | ΔC, % |
|---|---|---|---|
| Found, % | $1.4 \cdot 10^{-3}$ | $8.5 \cdot 10^{-4}$ | −40 |

TABLE 2

| Added, % | $2.0 \cdot 10^{-3}$ ($CaF_2$) | $2.0 \cdot 10^{-3}$ ($K_2ZrF_6$) | $5 \cdot 10^{-4}$ ($K_2ZrF_6$) |
|---|---|---|---|
| Found, % | $1.8 \cdot 10^{-3}$ | $2.2 \cdot 10^{-3}$ | $4.7 \cdot 10^{-4}$ |

The reproducibility of the results, evaluated from 30 spectrograms for zirconium samples containg $1.4 \cdot 10^{-3}$ % fluorine, is characterized by a mean square error of a single determination of ±17% (relative). Thus, the experimental error is ± 10% (relative) for three parallel determinations.

We were unable to check on the reliability of our results by comparing them with those of other methods, since there are no reliable methods for the determination of fluorine in metallic zirconium. In Table 2 are given results of experiments "added−found", from which it is clear that even in those cases where fluorine is contained in the test sample and in the standards in the form of different compounds, the amounts of fluorine added are found, with an error lying within the accuracy limits of the method.

It should be noted that the reproducibility for synthetic mixtures is somewhat lower than for metal samples. This is connected, presumably, with the unevenness of distribution of the salt introduced, following from the large difference in specific gravity and the degree of dispersion between it and the base material − filings of metallic zirconium. This is particularly the case when the standards are stored for a long time. Accordingly, bricketting should be carried out immediately after preparing the standards, and the standards should be stored in the form of brickettes.

When a zirconium sample containing a high content of fluorine is available, standard mixtures can be prepared by diluting it with zirconium iodide filings. The fluorine content of mixtures is established by analyzing them as carefully as possible on the basis of standards to which fluorine-containing salts have been added. When working with standards prepared by diluting a zirconium sample, the bricketting operation can be omitted.

When a triple-electrode discharge tube is used, it is possible to photograph the spectra and to calculate the results for 20-25 samples in a working day (3 parallel photographs for each sample). The preliminary operations require 7-10 min for each sample.

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## SUMMARY

Taking as an example the determination of small amounts of fluorine in metallic zirconium the possibility has been demonstrated of making analytical use of the secondary chemical reactions which occur under the special conditions appertaining to a high-temperature discharge in a hollow cathode.

A highly sensitive spectrographic method has been developed for the determination of fluorine in metallic zirconium.

## LITERATURE CITED

[1] Yu. I. Korovin and L. V. Lipis, Optika i Spektroskopiya 5, 334 (1958); Trans. Second International Conference on the Peaceful Uses of Atomic Energy, Geneva, 4, 1958, p. 316. [in Russian] (Izd. Upravl. po Ispol'z. Atomnaya Energiya, Moscow, 1959); Progress in nuclear energ. Analytical Chemistry, v. 1, p. 244; Pergamon Press, 1958.

[2] J. R. McNally, G. R. Harrison, and E. Rowe, J. Opt. Soc. Amer. 37, 93 (1947).

[3] M. P. Chaika, Optika i Spektroskopiya 2, 421 (1957).

[4] F. T. Birxs, Spectrochim. Acta 6, 169 (1954).

[5] W. R. Martini, A compilation of vapor pressure data for the elements from Br to U, and their oxides and carbides, NAA − SR − 215, 1953.

[6] G. L. Miller, Zirconium [Russian translation] (IL, Moscow, 1955).

[7] J. Papisch, L. E. Hoag, and W. E. Snee, Ind. Eng. Chem. Anal. Ed. 2, 263 (1930).

[8] A. W. Petrey, Ind. Eng. Chem. Anal. Ed. 6, 343 (1934).

[9] W. Paul, Angew. Chem. 49. 901 (1936).

[10] V. R. Ognev, Trudy Sibirsk Fiz. Tekh. Inst. Tomsk Universiteta 36, 1958, p. 281.

[11] P. E. Lemieux and R. H. Black, Spectrochim. Acta N 3/4, 291 (1959).

[12] S. Tolanskii, High-Resolution Spectroscopy [Russian translation] (IL, Moscow, 1955).

[13] V. M. Latimer, Oxidation States of Elements and Their Potentials in Aqueous Solutions [Russian translation] (IL, Moscow, 1954).

# CHEMICOSPECTROGRAPHIC DETERMINATION OF IMPURITIES IN LEAD

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At present, high-purity lead is being produced which contains 99.999% and upwards of this metal. It is known that impurities strongly affect the technological and physicochemical properties of the metal, and, accordingly, their amounts are limited by very firm specifications [1-5]. Determination of traces of many impurities by chemical methods presents considerable difficulties. In order to determine individual elements large aliquots of sample are necessary, in some instances even up to a kilogram [5-7].

Published spectrographic methods of analyzing lead provide for the determination of a series of impurities by exciting the spectrum in a spark or an arc between metallic electrodes, or in an arc between carbon electrodes filled with powdered lead compounds [8-15]. The sensitivity of direct spectrographic methods is not high enough for the analysis of high-purity lead.

A description is given below of a chemicospectrographic method developed in 1951 for the analysis of high-purity lead [16, 17]. The impurities are concentrated by separating the base element (lead) from a nitric acid solution in the form of sulfate. The concentrate of impurities obtained after evaporation of the decanted mother liquor in the form of $PbSO_4$ powder is subjected to spectrographic analysis. Twenty-four elements present as impurities are simultaneously determined with a sensitivity of $10^{-4} - 10^{-6}$ %.

Precipitation of lead as the sulfate is fairly selective and permits its separation from numerous elements which form soluble sulfates [18-20]. It should be noted that in a number of standard methods of analyzing lead, use is made of the separation of $PbSO_4$ from impurities which are then determined in the mother liquor by chemical methods [6, 7].

The conditions under which $PbSO_4$ is precipitated in the method we have developed differ from the conditions adopted in classical methods of analysis. Partial precipitation is effected from hot, dilute nitric acid solutions. The nitric acid present enhances the solubility of lead sulfate, and this favors the growth of crystals and the self-purification of the precipitate. The $PbSO_4$ precipitate separated from the mother liquor is additionally subjected to recrystallization by heating with 6 N nitric acid. The conditions chosen completely eliminate loss of test elements with the $PbSO_4$ precipitate. In order to confirm the quantitative concentration of traces of elements in the mother liquor, it was essential to study phase distribution in a system consisting of one macrocomponent (lead) and a large number of microimpurities. In experiments with synthetic mixtures of salts under the conditions chosen for precipitation of $PbSO_4$, a study was made of the distribution between the solid and liquid phases of the following impurities: Na, Ca, Mg, Ba, Sr, Al, Ti, V, Cr, Mn, Mo, Co, Ni, Sb, Zn, Cd, Cu, Fe, Bi, Sn, Ag, Au, In, Tl, Te, As. To a nitric acid solution of spectrographically pure lead nitrate was added standard solutions of all the elements, and $PbSO_4$ precipitated with sulfuric acid. The lead sulfate separated from the mother liquor by decantation, was washed by boiling with nitric acid and subjected to spectrographic analysis. The decanted mother liquor, which was combined with the wash nitric acid, was evaporated to dryness and

calcined. The concentrate of impurities obtained, the base of which is $PbSO_4$, was also analyzed spectrographically. In addition, the distribution of the individual elements between the phases were studied by means of the following radioactive isotopes: $Ca^{45}$, $Cr^{51}$, $Mo^{99}$, $Fe^{59}$, $Co^{60}$, $Cd^{115}$, $In^{114}$, $Sb^{124}$, $Sn^{113\,123}$, $Tl^{204}$, $Ag^{110}$, $Zn^{65}$, $Au^{198}$. The activity of the concentrates and the precipitates obtained, as well as that of the corresponding standards, was measured on a type B-2 setup with a TS-17 torsion counter. In these experiments, in order to take into account the screening effect of the $PbSO_4$ precipitate, the same amount of lead sulfate as that present on the targets containing the sample was placed on the standard targets. A study was made of the effect of the nitric acidconcentration of the solution, the aging of the precipitate, excess $Pb^{2+}$ or $SO_4^{2-}$ ions, recrystallization of the $PbSO_4$ precipitate, and concentrations of the partitioned microcomponents. The content of each element in synthetic mixtures was varied from $10^{-1}$ to $10^{-6}$ %, and for certain elements, down to $10^{-7}$ % with respect to lead.

Experiments involving chemical and spectrographic analysis, and also radioactive indicators, gave results in agreement with each other; on the basis of these results the partition coefficients of the impurity elements between the solid and liquid phases were calculated. The following impurities remain almost completely (85-100%) in the aqueous phase: Na, Ca, Mg, Al, Ti, V, Cr, Mn, Mo, Co, Ni, Sb, Zn, Cd, Cu, Fe, Bi, Sn, Ag, In, Te, As. It should be pointed out that the elements indicated form sulfates which are not isomorphous with lead sulfate. As one might expect, strontium and barium, whose sulfates are isomorphous with $PbSO_4$, were coprecipitated with the lead sulfate.

Analytical procedure. An aliquot of lead weighing 10 g is dissolved in 45 ml of 6 N $HNO_3$ on heating, water is added to the solution obtained to bring the volume to 100 ml. $PbSO_4$ is precipitated by adding 35 ml of 3.6 N $H_2SO_4$ to the solution which has been heated to about 80°; the precipitate is then kept in the solution for three hours at room temperature. The mother liquor is removed by decantation and the lead sulfate recrystallized by heating with 40 ml of 6 N $HNO_3$ for two hours. The mother liquor which is combined with wash nitric acid is evaporated to dryness in a tared quartz basin. The powder thereby obtained, the base of which is $PbSO_4$, is calcined for 30 min at 550° and weighed. The enrichment coefficient of the impurities in the concentrate is calculated by means of the formula:

$$K = M/m \cdot 0{,}683$$

where M is the weight of lead taken (in g); m is the weight of concentrate (in g); 0.683 is the factor for converting $PbSO_4$ to Pb.

A sample in which chemical enrichment is not used is prepared by dissolving 1 g of lead or its compound in 20 ml of 6 N $HNO_3$. In order to convert the sample into the sulfate, the solution is diluted with water to 30 ml, and 6 ml of 18 N $H_2SO_4$ added. The solution plus precipitate is evaporated to dryness and calcined at 550°. In parallel to preparation of a sample for analysis, control experiments are carried out separately for concentrates and samples not enriched, using spectrographically pure lead sulfate.

All chemical operations are carried out in a vessel made of transparent quartz. The water and acids used are distilled beforehand in a quartz apparatus.

Spectrographic determination of impurities. The spectra of the chemical concentrate, the samples which have not been enriched, control experiments, and standard are photographed on the same photographic plate under identical conditions. The simultaneous photography of samples which have not been enriched is carried out for two reasons: firstly, those impurities which are not concentrated are determined in the sample which has not been enriched; secondly, the concentration range which can be encompassed can be extended appreciably using only one series of standards.

Spectrum excitation conditions: dc arc, 13 amp current; the lower electrode is a carbon rod with a crater 4.5 mm in diameter and 6 mm deep; the upper electrode is a rod sharpened to a cone. The amount of powder placed in the electrode crater is 100 mg. Exposure time 2.5 min; during this time complete evaporation of the sample in the arc discharge occurs. Photographic plates, spectrographic type II, spectrograph ISP-22, slit width 10 $\mu$. A two-stage attenuator with relative transmission coefficients of 0.8 and 2.00 are fixed in front of the slit. In order to determine the impurities quantitatively, the method of constructing a calibration curve by means of standards within the coordinates log I, log C, using a calculating machine, is adopted. For the

TABLE 1

Analytical Lines and the Sensitivity of Determination of Impurities in Lead (the content of the elements is expressed as % wt. on lead)

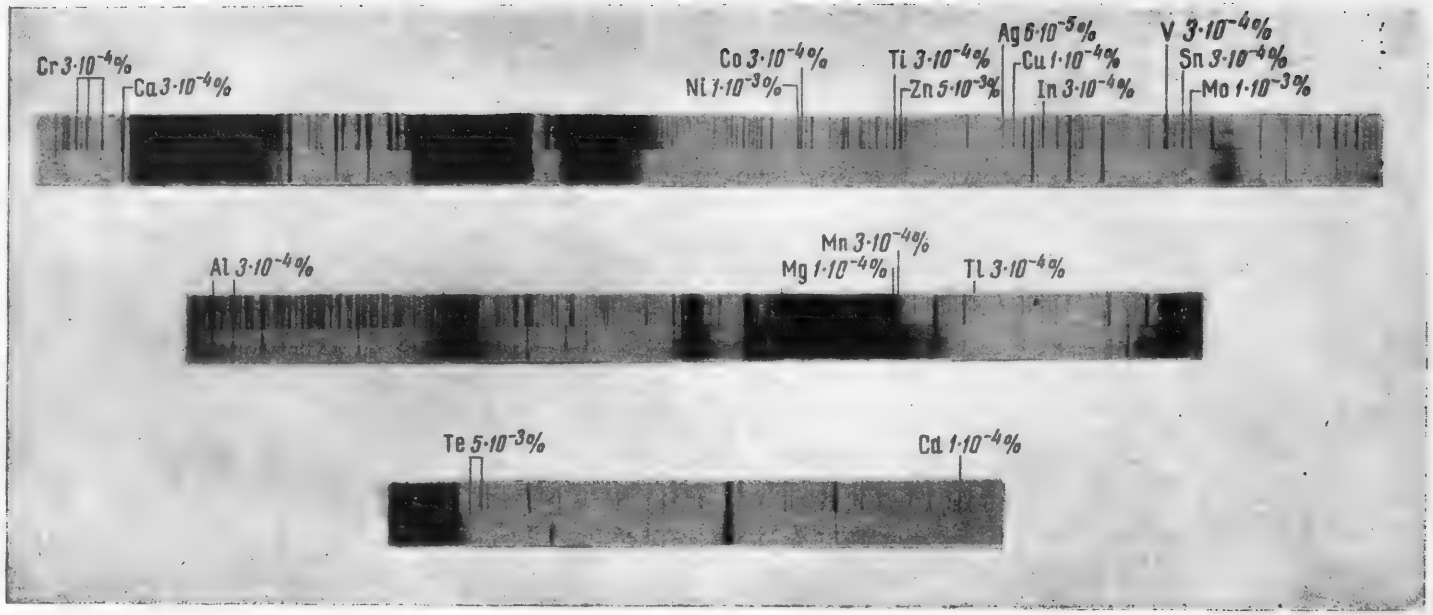
| Element and its analytical line | Sensitivity* | | Element and its analytical line | Sensitivity* | |
|---|---|---|---|---|---|
| | not enriched | after concentration | | not enriched | after concentration |
| Mg 2795,5 | $2 \cdot 10^{-4}$ | $5 \cdot 10^{-5}$ | Ni 3050,8 | $1 \cdot 10^{-3}$ | $3 \cdot 10^{-5}$ |
| Ca 4226,7 | $1 \cdot 10^{-3}$ | $5 \cdot 10^{-5}$ | Cu 3247,5 | $1 \cdot 10^{-4}$ | $3 \cdot 10^{-6}$ |
| Ba 2335,3 4934,1 | $1 \cdot 10^{-3}$ | — | Ag 3280,7 | $3 \cdot 10^{-5}$ | $1 \cdot 10^{-6}$ |
| | | | Zn 2138,6 | $3 \cdot 10^{-3}$ | $1 \cdot 10^{-4}$ |
| Al 3082,2 | $3 \cdot 10^{-4}$ | $5 \cdot 10^{-5}$ | Cd 2288,0 | $1 \cdot 10^{-4}$ | $3 \cdot 10^{-6}$ |
| Ti 3349,0 | $1 \cdot 10^{-3}$ | $3 \cdot 10^{-5}$ | In 3256,1 | $3 \cdot 10^{-4}$ | $1 \cdot 10^{-5}$ |
| V 3185,4 | $2 \cdot 10^{-4}$ | $6 \cdot 10^{-6}$ | Sn 3175,0 | $1 \cdot 10^{-3}$ | $3 \cdot 10^{-5}$ |
| Cr 4254,3 | $3 \cdot 10^{-4}$ | $1 \cdot 10^{-5}$ | Sb 2598,1 | $1 \cdot 10^{-2}$ | $3 \cdot 10^{-4}$ |
| Mo 3909,0 | $1 \cdot 10^{-3}$ | $3 \cdot 10^{-5}$ | Bi 2898,0 | $1 \cdot 10^{-3}$ | $3 \cdot 10^{-5}$ |
| Mn 2794,8 | $3 \cdot 10^{-5}$ | $1 \cdot 10^{-6}$ | Te 2383,3 | $5 \cdot 10^{-3}$ | $2 \cdot 10^{-4}$ |
| Fe 2719,0 | $3 \cdot 10^{-4}$ | $1 \cdot 10^{-4}$ | As 2349,8 | $5 \cdot 10^{-3}$ | $2 \cdot 10^{-4}$ |
| Co 3412,6 | $6 \cdot 10^{-4}$ | $2 \cdot 10^{-5}$ | Au 2428,0 | $5 \cdot 10^{-3}$ | — |

* The sensitivity for the determination of Mg, Ca, Al, and Fe is given after corrections for the control experiment.

TABLE 2

Checking the Method Developed on Synthetic Mixtures (as % wt. on lead)

| Test element | Mixture I | | Mixture II | | Mixture III | |
|---|---|---|---|---|---|---|
| | added | found | added | found | added | found |
| Mg | $5 \cdot 10^{-5}$ | $5,9 \cdot 10^{-5}$ | $1 \cdot 10^{-2}$ | $1 \cdot 10^{-2}$ | $5 \cdot 10^{-5}$ | $7,3 \cdot 10^{-5}$ |
| Ca | $5 \cdot 10^{-4}$ | $4 \cdot 10^{-4}$ | $1 \cdot 10^{-2}$ | $8 \cdot 10^{-3}$ | $2 \cdot 10^{-4}$ | $2,2 \cdot 10^{-4}$ |
| Al | $5 \cdot 10^{-4}$ | $4,2 \cdot 10^{-4}$ | $1 \cdot 10^{-2}$ | $1,2 \cdot 10^{-2}$ | $2 \cdot 10^{-4}$ | $4 \cdot 10^{-4}$ |
| Ti | $5 \cdot 10^{-5}$ | $3 \cdot 10^{-4}$ | $3 \cdot 10^{-2}$ | $3,6 \cdot 10^{-2}$ | $2 \cdot 10^{-4}$ | $4,8 \cdot 10^{-4}$ |
| V | $5 \cdot 10^{-4}$ | $4,4 \cdot 10^{-4}$ | $3 \cdot 10^{-2}$ | $3 \cdot 10^{-2}$ | $2 \cdot 10^{-4}$ | $2 \cdot 10^{-4}$ |
| Cr | $5 \cdot 10^{-4}$ | $4 \cdot 10^{-4}$ | $1 \cdot 10^{-2}$ | $1,3 \cdot 10^{-2}$ | $2 \cdot 10^{-4}$ | $1,8 \cdot 10^{-4}$ |
| Mo | $5 \cdot 10^{-4}$ | $4 \cdot 10^{-4}$ | $1 \cdot 10^{-2}$ | $1 \cdot 10^{-2}$ | $2 \cdot 10^{-4}$ | $2,5 \cdot 10^{-4}$ |
| Mn | $5 \cdot 10^{-5}$ | $4,7 \cdot 10^{-5}$ | $1 \cdot 10^{-2}$ | $1,2 \cdot 10^{-2}$ | $5 \cdot 10^{-5}$ | $4,2 \cdot 10^{-5}$ |
| Fe | $5 \cdot 10^{-4}$ | $3,6 \cdot 10^{-4}$ | $3 \cdot 10^{-2}$ | $3,5 \cdot 10^{-2}$ | $2 \cdot 10^{-4}$ | $2,2 \cdot 10^{-4}$ |
| Co | $5 \cdot 10^{-4}$ | $3,8 \cdot 10^{-4}$ | $1 \cdot 10^{-3}$ | $1,3 \cdot 10^{-3}$ | $2 \cdot 10^{-4}$ | $2,9 \cdot 10^{-4}$ |
| Ni | $5 \cdot 10^{-4}$ | $4,2 \cdot 10^{-4}$ | $3 \cdot 10^{-3}$ | $3 \cdot 10^{-3}$ | $2 \cdot 10^{-4}$ | $2,7 \cdot 10^{-4}$ |
| Cu | $5 \cdot 10^{-5}$ | $2 \cdot 10^{-5}$ | $1 \cdot 10^{-2}$ | $1,1 \cdot 10^{-2}$ | $5 \cdot 10^{-5}$ | $1 \cdot 10^{-4}$ |
| Ag | $5 \cdot 10^{-5}$ | $5,6 \cdot 10^{-5}$ | $1 \cdot 10^{-4}$ | $1,1 \cdot 10^{-4}$ | $2 \cdot 10^{-4}$ | $1,2 \cdot 10^{-4}$ |
| Zn | $5 \cdot 10^{-3}$ | $6,4 \cdot 10^{-3}$ | $3 \cdot 10^{-2}$ | $3,5 \cdot 10^{-2}$ | $2 \cdot 10^{-4}$ | $2\ 8 \cdot 10^{-4}$ |
| Cd | $1 \cdot 10^{-4}$ | $7 \cdot 10^{-5}$ | $1 \cdot 10^{-2}$ | $1,1 \cdot 10^{-2}$ | $5 \cdot 10^{-5}$ | $3 \cdot 10^{-5}$ |
| In | $5 \cdot 10^{-5}$ | $5 \cdot 10^{-5}$ | $1 \cdot 10^{-2}$ | $1 \cdot 10^{-2}$ | $5 \cdot 10^{-5}$ | $6,7 \cdot 10^{-5}$ |
| Sn | $5 \cdot 10^{-4}$ | $2,2 \cdot 10^{-4}$ | $1 \cdot 10^{-2}$ | $1 \cdot 10^{-2}$ | $2 \cdot 10^{-4}$ | $2,2 \cdot 10^{-4}$ |
| Sb | $5 \cdot 10^{-3}$ | $4,7 \cdot 10^{-3}$ | $3 \cdot 10^{-1}$ | $5,1 \cdot 10^{-1}$ | $2 \cdot 10^{-3}$ | $2,4 \cdot 10^{-3}$ |
| Bi | $5 \cdot 10^{-4}$ | $5,7 \cdot 10^{-4}$ | $1 \cdot 10^{-2}$ | $1,2 \cdot 10^{-2}$ | — | — |
| Te | — | — | $1 \cdot 10^{-2}$ | $8 \cdot 10^{-3}$ | $1 \cdot 10^{-3}$ | $7 \cdot 10^{-4}$ |
| As | $1,6 \cdot 10^{-4}$ | $1,5 \cdot 10^{-4}$ | $5 \cdot 10^{-3}$ | $7,5 \cdot 10^{-3}$ | $5 \cdot 10^{-3}$ | $7,7 \cdot 10^{-3}$ |
| Au | $1 \cdot 10^{-4}$ | $1,6 \cdot 10^{-4}$ | $3 \cdot 10^{-4}$ | $2,8 \cdot 10^{-4}$ | — | — |




Comparison of a spectrogram (a) for a sample of lead in the form of $PbSO_4$ with a spectrogram (b) for a concentrate of the impurities from the same lead sample on the same base for an enrichment coefficient K = 30.

analysis of the concentrate of impurities, the result obtained from the calibration curve is divided by the enrichment coefficient, in order to find the amount of a given impurity in the sample. Using one photographic plate the following elements are quantitatively determined separately: Ca, Mg, Al, Ti, V, Cr, Mn, Mo, Co, Ni, Sb, Zn, Cd, Cu, Fe, Bi, Sn, Ag, In, Te, As, Ba, Sr, Au. Determination of arsenic is carried out by means of a separate series of standards in view of the superposition of the analytical lines of Cd and As. Ba, Sr, and Au are only determined in samples which have not been enriched.

Thanks to the chemical enrichment of the impurities, the sensitivity of the method is increased 30-100 times as compared with the direct spectrographic method of analysis. Results on the sensitivity of the method are given in Table 1; the effect of enrichment of impurities on the increase in sensitivity is evident from the diagram. The accuracy and reproducibility of the method were checked on numerous synthetic mixtures which were prepared by adding all the elements indicated to a solution of spectrographically pure lead nitrate. The mixtures were analyzed by the method indicated above. The experimental accuracy depends on the concentration range, and differs for the various impurities. For impurities present in amounts of the order of $10^{-4}$%, the accuracy is characterized by a relative error of ± 20% (Table 2).

The standards used for the spectrographic analysis were prepared on the basis of spectrographically pure lead sulfate by adding appropriate amounts of standard solutions of the elements.

## SUMMARY

A chemicospectrographic method has been developed for the determination of impurities in lead and its compounds; it is based on the combination of a preliminary chemical concentration and subsequent spectrographic analysis.

The impurities are concentrated 30-100 times by removing lead from nitric acid solution in the form of its sulfate. The concentrate which is obtained on a lead sulfate base is subjected to spectrographic analysis simultaneously with a sample which has not been enriched, using the same standards.

A study has been made of the behavior of traces of elements, and of their distribution between liquid and solid phase under the experimental conditions. It has been shown that the elements: Na, Ca, Mg, Al, Ti, V, Cr, Mn, Mo, Co, Ni, Sb, Zn, Cd, Cu, Fe, Bi, Sn, Ag, In, Te, As are not coprecipitated over a wide concentration range (from $10^{-1}$ to $10^{-6}$%) with the lead sulfate precipitate under the experimental conditions used.

The method developed permits the simultaneous determination of 24 elements with a sensitivity of $10^{-4}$ – $10^{-6}$% with a relative error of ± 20%. The method can be used for controlling high-purity lead.

## LITERATURE CITED

[1] Reference Book on the Metallurgy of Nonferrous Metals, Edited by N. N. Murach [in Russian] (Metallurgizdat, Moscow, 1953) p. 1101.

[2] M. P. Slavinskii, Physicochemical Properties of the Elements [in Russian] (Metallurgizdat, Moscow, 1952) p. 325.

[3] GOST 3378-47, Lead, Classification and Technical Conditions.

[4] A. E. van Arkel, Reine Metalle, Berlin, 1939, S. 501.

[5] R. C. Hughes, Spectroch. Acta 5, 210 (1952).

[6] Analyse der Metalle, B. 1, Schiedsverfanren, Berlin, 1949, p. 85.

[7] Berl Lunge, Chemicotechnological Methods of Research 2, Part 2 [Russian translation] (Goskhimizdat, Moscow-Leningrad, 1938) p. 308.

[8] K. N. Taganov, Zavodskaya Lab. 12, 449 (1946).

[9] A. E. Zak, Izvest. Akad. Nauk SSSR, Seriya Fizich. 12, 463 (1948).

[10] A. I. Alekseeva, Zavodskaya Lab. 15, 700 (1949).

[11] A. Larsson, Ierucontorets ann. 137, 194 (1953).

[12] M. É. Britske, N. D. Zdanovich, et al., Collection, Metallurgy and Enrichment of Nonferrous Metals [in Russian] (Metallurgizdat, Moscow, 1953) p. 99.

[13] Hanafusa Tomita, J. Japan Soc. Test. Mater. 6, N 42, 157 (1957); Ref. Zhur. Khim. N 24 (1957).

[14] I. G. Yudelevich, V. G. Kovaleva, and A. P. Levitina, Zavodskaya Lab. 22, 1310 (1956).

[15] I. G. Yudelevich and V. G. Kovaleva, Zavodskaya Lab. 24, 461 (1958).

[16] A. G. Karabash and Sh. I. Peizulaev, Collection, Preparation of Isotpoes. Power Gamma Setups. Radiometry and Dosimetry [in Russian] (Izd. AN SSSR, Moscow, 1958) p. 36.

[17] A. G. Karabash, Sh. I. Peizulaev, et al., Materials of the Tenth Conference on Spectroscopy, 2 [in Russian] (L'vov University, 1958) p. 556.

[18] W. F. Hillebrand, G. E. Lundell, H. A. Bright, and J. I. Hoffman, Practical Textbook on Inorganic Analysis [Russian translation] (Goskhimizdat, Moscow, 1957) p. 234.

[19] A. Seidell, Solubilities of Inorganic and Metallorganic Compounds (New York, 1948) p. 1409.

[20] Chemist's Notebook 1, [in Russian] (Goskhimizdat, Leningrad-Moscow, 1951) p. 300.

# ANALYSIS OF FLUOROORGANIC COMPOUNDS. SIMULTANEOUS MICRODETERMINATION OF FLUORINE, CARBON, AND HYDROGEN IN LOW-BOILING AND GASEOUS COMPOUNDS

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The present article is devoted to a description of the application of a method for the simultaneous determination of fluorine, carbon, and hydrogen [1-3] to the analysis of low-boiling and gaseous fluoroorganic compounds. The basic difficulties in the analysis of such materials are connected with taking samples and the introduction of samples into the combustion tube. Several methods have been described in the literature for the analysis of volatile liquids. In most cases a capillary containing an aliquot is sealed up and it is then opened either in the combustion tube itself by means of various gadgets, or it is opened immediately before being introduced into the tube [4-13]. Vessels of special design have also been suggested which are connected to the combustion tube and serve for breaking the ampoule containing the sample, and for mixing the vapors of the test material with oxygen [14-17]. As we have mentioned already [3], during the combustion of fluoroorganic liquids in a magnesium oxide layer, the use of glass capillaries for holding the sample is not desirable, since contamination of the magnesium oxide by lumps of fused glass can lead to damage of the apparatus and to incorrect experimental results. Accordingly, for the analysis of high-boiling liquids we used a quartz capillary, the end of which was left open. The weight of the capillary plus aliquot hardly changes even when the test liquid has a boiling point less than 100°.

Since, on taking samples in an open quartz capillary, combustion of a liquid is no more complicated than combustion of solid materials, it was interesting to check on the possibility of using such a capillary for the analysis of low-boiling liquids as well. As long ago as 1932, Pirsch [18] found that an aliquot of diethyl ether does not lose weight as long as the liquid layer in the capillary is separated from the surrounding medium by a few cubic millimeters of air found in the narrow end of the capillary. We established that the weight of various volatile liquids remained constant in a series of quartz capillaries the diameter of the open end of which was 0.2-0.3 mm. As can be seen from the results given in Table 1, thanks to the small diameter of the open end of the capillary and the small evaporation surface the losses following upon volatilization are comparatively small, are readily reproducible, and are constant with time.

In those cases where loss of the test material is appreciable, as for example, during the analysis of pentafluoropropane, knowing the change in weight of capillary plus sample per unit time, and the time which elapses between reading the balance and introducing the capillary plus test material into the combustion tube, it is possible to calculate how many micrograms it is necessary to subtract from the weight taken.

* Deceased.

TABLE 1

Weighing of Volatile Materials in Open Capillaries

| B. p. of material, °C | First reading, mg | Readings made after definite time intervals after the first reading, mg | | | | | | Change in weight in one minute,* mg |
|---|---|---|---|---|---|---|---|---|
| | | minutes | | | | | | |
| | | 1 | 2 | 3 | 4 | 5 | 10 | |
| 78,4 | 3,195 | 3,195 | 3,195 | 3,195 | 3,195 | 3,195 | 3,192 | 0,000 |
| 56 | 1,225 | 1,220 | 1,218 | 1,212 | 1,210 | 1,205 | 1,188 | —0,004 |
| | 9,210 | 9,208 | 9,200 | 9,192 | 9,188 | 9,182 | 9,155 | —0,006 |
| 34,6 | 7,125 | 7,120 | 7,112 | 7,103 | 7,103 | 7,100 | 7,080 | —0,004 |
| | 1,570 | 1,566 | 1,558 | 1,552 | 1,547 | 1,541 | 1,516 | —0,005 |
| 27 | 3,430 | 3,420 | 3,412 | 3,401 | 3,900 | 3,980 | 3,970 | —0,010 |
| | 5,160 | 5,151 | 5,139 | 5,130 | 5,120 | 5,110 | 5,101 | —0,010 |
| 20 | 3,150 | 3,128 | 3,102 | 3,080 | — | — | — | —0,023 |
| | 4,160 | 4,135 | 4,111 | 4,088 | — | — | — | —0,024 |

* Balance room temperature about 20°.

TABLE 2

Determination of Fluorine, Carbon, and Hydrogen in Volatile Materials, Samples on Which Were Taken in Open Capillaries

| Test material | B. p. | C, % | | H, % | | F, % | |
|---|---|---|---|---|---|---|---|
| | | found | difference | found | difference | found | difference |
| 1-Ethylperfluoroisobutylene $C_6H_5F_7$ | 75° | 34,36 | +0,07 | 2,53 | +0,18 | 63,70 | +0,40 |
| | | 34,41 | +0,12 | 2,66 | +0,26 | 63,40 | +0,10 |
| Calculated: C = 34.29%; H = 2.40%; F = 63.30% | | | | | | | |
| 1-Bromo-2-hydroperfluoroisobutane $C_4HBrF_8$ | 56° | 17,23 | +0,13 | 0,39 | +0,04 | 54,15 | +0,06 |
| | | 17,19 | +0,09 | 0,38 | +0,03 | 53,82 | +0,27 |
| Calculated: C = 17.10%; H = 0.35%; F = 54.09% | | | | | | | |
| 3,3,3,1-Tetrafluoro-2-trifluoroisobutane $C_4H_3F_7$ | 40° | 26,10 | +0,02 | 1,66 | +0,04 | 72,29 | +0,01 |
| | | 25,93 | —0,10 | 1,53 | —0,09 | 72,03 | —0,20 |
| Calculated: C = 26.08%; H = 1.62%; F = 72.28% | | | | | | | |
| 1,2-Dihydroperfluoroisobutane $C_4H_2F_8$ | 35° | 23,88 | +0,12 | 1,15 | +0,16 | 74,91 | —0,33 |
| | | 23,91 | +0,15 | 1,06 | +0,07 | 74,74 | —0,50 |
| Calculated: C = 23.76%; H = 0.99%; F = 75.24% | | | | | | | |
| 3,3,3,2,1-Pentafluoropropane $C_4H_3F_5$ | 20° | 26,96 | +0,12 | 2,45 | +0,22 | 70,41 | —0,47 |
| | | 26,96 | +0,12 | 2,50 | +0,27 | 70,57 | —0,31 |
| Calculated: C = 26.84% H = 2.23%; F = 70.88% | | | | | | | |

Note: All the analyses were carried out on samples of 4-8 mg.

Table 2 contains analytical results for liquid materials, aliquots of which were taken in open capillaries. It should be noted, however, that considerable skill is required on the part of the analyst when dealing with materials boiling at 20°, while for materials which are gaseous at room temperature, the method described above for taking samples cannot be, in general, used.

Samples of gaseous compounds can be taken either by volume – by means of a gas buret – or by weight – in a sealed glass capillary. The latter technique has the advantage that the percentage content of the elements in the aliquot can be calculated, without having to know the specific gravity of the material; however, it is only suitable for readily condensed gases which boil within the temperature range +20° to −45°. For reasons

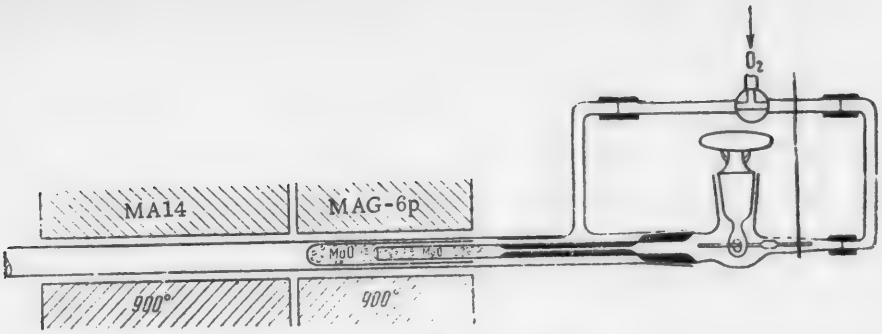


Fig. 1.

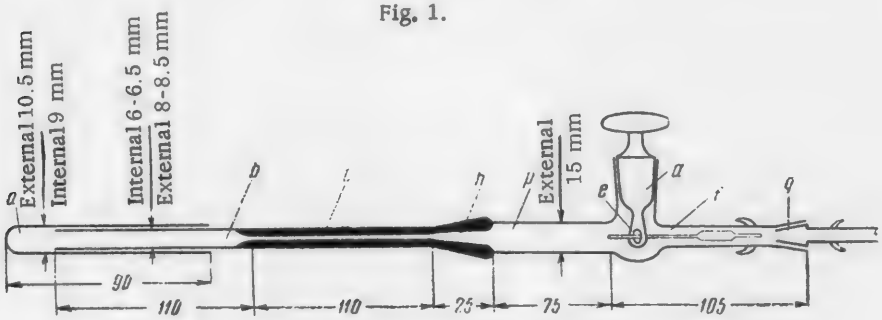


Fig. 2.

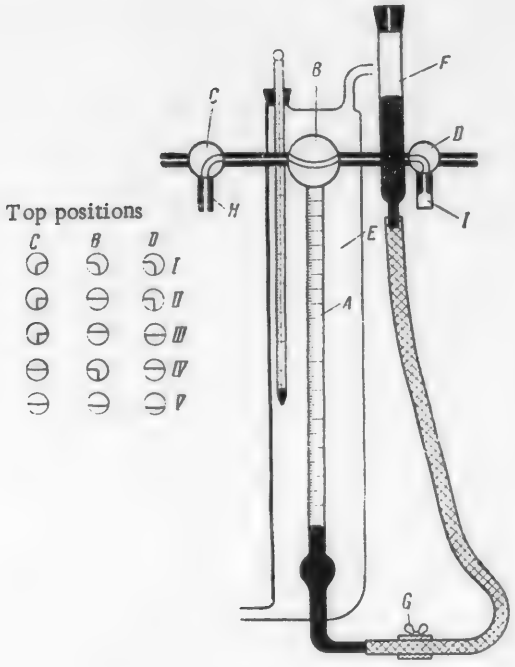


Fig. 3.

reasons outlined before [3], a capillary containing an aliquot cannot be opened in the magnesium oxide layer, and, consequently, in this case it is necessary to break it inside the combustion tube.

Of the known methods used for this purpose we chose the "tap opener" suggested by Yu. N. Dagaevaya and K. I. Novozhilova. The end of the sealed capillary is placed in a hole in the barrel of a tap fitted between

TABLE 3

Determination of Fluorine, Carbon, and Hydrogen in Gases

| Test material | B. p. | C, % | | H, % | | F, % | |
|---|---|---|---|---|---|---|---|
| | | found | difference | found | difference | found | difference |
| Monohydroperfluoroisobutylene $C_4HF_7$ Calculated: C = 26.37% H = 0.54%; F = 73.02% | +18° | 26,06** | —0,31 | 0,64 | +0,10 | 73,13 | +0,11 |
| | | 26,08** | —0,29 | 0,67 | +0,13 | 72,89 | +0,13 |
| Monohydroperfluoroisobutane $C_4HF_9$ Calculated: C = 21.83%; H = 0.46%; F = 77.71% | +13° | 21,62** | —0,21 | 0,53 | +0,07 | 77,76 | +0,05 |
| | | 21,70** | —0,13 | 0,42 | +0,04 | 77,60 | —0,11 |
| 3,3,3,2,1,1-Hexafluoropropane $C_3H_2F_6$ Calculated: C = 23.67%; H = 1.31%; F = 75.00% | +5° | 23,33** | —0,34 | 1,28 | —0,03 | 74,53 | —0,47 |
| | | 23,30** | —0,37 | 1,23 | —0,08 | 74,93 | —0,07 |
| Monohydroperfluoropropane $C_3HF_7$ Calculated: C = 21.17%; H = 0.59%; F = 78.23% | —17° | 21,13** | —0,04 | 0,46 | —0,13 | 77,92 | —0,31 |
| | | 20,95** | —0,22 | 0,57 | —0,02 | 78,52 | +0,29 |
| 3,3,3,2,1-Pentafluoropropene-1 $C_3HF_5$ Calculated: C = 27.27%; H = 0.75%; F = 71.97% | —20° | 26,98** | —0,29 | 0,90 | +0,15 | 72,04 | +0,07 |
| | | 27,21** | —0,06 | 0,79 | +0,04 | 71,71 | —0,26 |
| Hexafluoroazoxymethane $C_2F_6N_2O$ Calculated: C = 13.19% F = 62.63% | +8° | 13,16* | —0,03 | 0 | 0 | 62,34 | —0,29 |
| | | 13,31** | +0,12 | 0,15 | +0,15 | 62,36 | —0,27 |
| Trifluoronitromethane $CF_3NO_2$ Calculated: C = 10.44% F = 49.56% | —31,2° | 10,43* | —0,01 | 0,07 | +0,07 | 49,60 | +0,14 |
| | | 10,60** | +0,16 | 0,09 | +0,09 | 49,39 | —0,17 |
| Difluorochloromethane $CHClF_2$ Calculated: C = 13.89%; H = 1.17%; F = 43.95% | —40° | 13,78* | —0,11 | 1,10 | —0,07 | 44,15 | +0,20 |
| | | 13,69** | —0,20 | 1,20 | +0,03 | 43,95 | 0 |
| 3,3,3-Trifluoropropine-1 $C_3HF_3$ Calculated: C = 38.31% H = 1.07%; F = 60.61% | —46° | 38,24* | —0,07 | 1,17 | +0,10 | 60,52 | —0,09 |
| | | 38,46** | +0,15 | 1,16 | +0,09 | 60,24 | —0,37 |
| 1,1,2-Trifluoroethene $C_2HF_3$ Calculated: C = 29.28% H = 1.22%; F = 69.48% | —51° | 29,45* | +0,17 | 1,17 | —0,05 | 69,72 | +0,24 |
| | | 29,40** | +0,12 | 1,12 | —0,10 | 69,30 | —0,18 |

Note: All analyses were carried out on 4-9 mg samples.

* The analysis was carried out by means of a gas buret.

** The analysis was carried out by means of a capillary opener.

the combustion tube and the apparatus used for preliminary purifying of the oxygen (Fig. 1). On rotating the tap the capillary is broken and the liquid is blown by the oxygen stream into the combustion tube. This apparatus had the drawback that on opening the capillary tube the test liquid fell on the tap barrel and thereby led to possible losses of material. We have improved the design of this tap, by placing the tap in the top part of the apparatus, thereby eliminating the drawback indicated above. An added advantage of this design for the tap (Fig. 2) is that the capacity of the widened part of the capillary which is located under the tap coupling can be increased where it is necessary that the test materials be copiously diluted with oxygen for safe combustion.

Materials which boil at temperatures below +20° can also be analyzed by means of a gas buret (Fig. 3). Table 3 contains the results obtained during the analysis of gaseous materials, when various methods of taking samples were used.

Below is given a description of those stages in the analysis of volatile and gaseous compounds which differ from the corresponding stages in the analysis of solid materials described earlier [3].

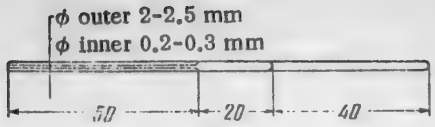


Fig. 4.

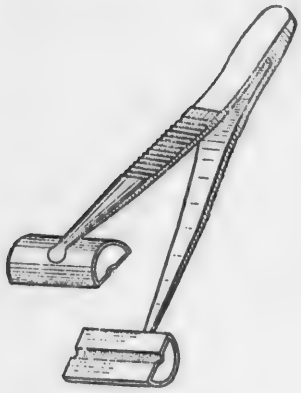

Fig. 5.

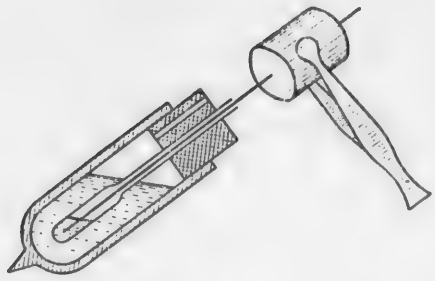

Fig. 6.

Analysis of volatile liquids boiling above 20°. Samples are taken in a quartz capillary (Fig. 4). In order to suck the liquid into the widened part of the capillary and to create an air stopper (blanket) in the narrow end, the capillary reservoir is cooled by means of special tongs which have cold compartments (Fig. 5).

The tongs with cold compartments can be constructed by fusing on to ordinary tongs hollow, brass, semicylindrical compartments with small longitudinal channels on the clamping surfaces, which enable the capillary to be held reliably. Lumps of dry ice are placed in the cooling compartments. When an aliquot is located in the bottom of the widened part of the capillary, no movement of the aliquot along the capillary is observed during weighing.

Analytical procedure. Before introducing the aliquot, that part of the combustion tube where the calcined magnesium oxide to be used for successive determinations is located is cooled with dry ice. The quartz capillary plus aliquot are placed in a tube and is strewn with magnesium oxide and is introduced into the combustion tube so that the closed end of the tube is in the cooled zone. At the beginning of combustion, the cooled part of the tube is insulated from heat by means of an asbestos screen. Then, as the electric oven is moved forward, cooling is removed and the analysis is finished as usual by gradually moving the oven onto the whole layer of magnesium oxide. A combustion lasts about 20 min.

Analysis of materials boiling in the range +20 to −45°. Into a small Dewar vessel fixed in an inclined position, and containing a cooling mixture whose temperature is a few degrees lower than the boiling point of the test material, is introduced a sealed ampoule containing the test material, the ampoule itself being fitted into a rubber bung with two holes. After the ampoule has been immersed for 3-5 min, the drawn-out end which sticks out through the rubber bung is cut and broken. The widened part of a thick-walled glass capillary which has been weighed beforehand is gently warmed over a flame and the drawn-out part of the capillary in the test liquid; the widened part of the capillary is held by means of the tongs with the cooled compartments (Fig. 6). When enough liquid has collected in the capillary, its drawn-out end is withdrawn from the ampoule, and is sealed, while the widened part is still held in the cooled compartments of the tongs. Using the simple gadgets described it is possible to take a sample in such a way that it is all found in the widened part of the capillary.

The sample is introduced into the combustion tube by means of the capillary breaker (Fig. 2) which is a quartz tap d with a stopper which terminates in a loop e. On one side of the tap is fused a tube f through which the sealed capillary containing the sample is introduced, while on the other side is fused a widened tube p, which is connected via the capillary c with the tube b filled with magnesium oxide. Combustion of the test material occurs in tube b. The capillary breaker is connected to the combustion tube (Fig. 1) through a joint h which is not lubricated. It could be connected by means of a rubber bung, but this is not so convenient. The ground joint of the tap is lubricated with silicone grease.

In the case of these low-boiling liquids, approximately one and a half times more magnesium oxide is used than for the analysis of solid and high-boiling fluorides [3]. A blank run is made at the beginning of a working day. Magnesium oxide which has been pyrohydrolyzed beforehand is then strewn into tube a (Fig. 2), and

from tube a into tube b. Tube a in which some magnesium oxide is left is fitted onto tube b so that a continuous MgO layer 9-10 cm long is obtained; the capillary breaker is connected by means of the joint h to the combustion tube and one of the capillaries containing a sample is placed in f so that the drawn-out end fits into the loop 3 in tap d. The joint g is connected to an oxygen supply, and, while the absorption apparatus is being weighed [3], the magnesium oxide is calcined, by moving the oven onto the tube and passing oxygen through the capillary breaker only (Fig. 1). The absorption apparatus is now connected to the combustion tube and the oven moved slightly in the direction of the oxygen stream, so that tube b containing the magnesium oxide sticks out from the oven a distance of 2 cm, while the rest of the magnesium oxide is in the calcined zone. In order to prevent heating of capillary c, an asbestos screen which presses tightly on the electric heater is fitted on the combustion tube; the aspirator tap is opened and that part of the capillary breaker in which the widened part of the capillary is located is cooled with dry ice, tube p is also cooled. After 2-3 min the capillary tip is broken by rotating the tap d, and the test material allowed to issue slowly from the capillary, the rate at which it issues being controlled by alternately applying and removing the cooling. This process takes about 15 min. When all the test material has come out of the capillary, cooling is stopped and all the magnesium oxide is calcined for 7-10 min. Next, by rotating the three-way tap, the oxygen stream is switched into the side entrance of the combustion tube, after a further 5-7 min the absorption apparatus is disconnected, the capillary breaker is switched off, all the magnesium oxide is strewn into the tube a, and the latter is transferred into the pyrohydrolysis tube as described previously [3].

Combustion as a whole takes about 25-30 min when the oxygen throughput is 20-25 ml/min.

Analysis of materials boiling below −45°. Gases boiling below −45° are sampled by means of the usual type of gas buret A (Fig. 3) having a volume of 2 ml. One filling of the buret is sufficient for 1-2 determinations. The buret is permanently connected into the setup used for carbon determination, between the capillary breaker and the gas-purifying system (Fig. 1). When the analyst is not working with a capillary breaker, it is necessary to have a similar following connecting quartz tube without a tap. The buret is provided with a crescent tap B by means of which it is possible either to introduce the gas to be analyzed or oxygen into the combustion tube, and with two additional taps C and D which allow the buret to be filled with gas without disconnecting it from the apparatus. Water from a thermostat is introduced into the water-jacket E of the buret. The zero reading of the buret is located at the tap B. The buret is filled with mercury or gas by means of bulb F and the screw clip G.

When sampling, the gas passes into the buret either directly from a cylinder, or from a gas pipet. The bulb F containing mercury is fixed in a position above tap B, the tap is turned to position I (Fig. 3), and, by opening clip G, the graduated part of the buret gradually filled with mercury; tap B is turned to position II and the clip closed. The gas inlet tube of the cylinder or a gas pipet is connected to the outlet H and gas passed through taps C, B, and D for 1/2 minute. During this operation the small drop of mercury which has entered into the opening in tap B during the operation of filling the buret is blown out by the gas stream into outlet I and is removed. The bulb F is then lowered, the clip G is opened slightly, and, by careful rotation of tap B into position I the gas is slowly let into the buret, after which tap B is turned back again into position II, and oxygen passed through all three taps (position III). During this operation the volume of the gas is read off at atmospheric pressure, and after setting the taps in position IV combustion is started.

At the beginning of a working day a blank run is carried out, oxygen being passed through the side entry of the combustion tube. While the buret is being filled with test gas, and after the blank run has been carried out, oxygen is passed through taps B, D, and C. The magnesium oxide is then prepared as indicated above; the weighed absorption apparatus is connected to the combustion tube and combustion of the gas commenced. For this purpose, bulb F containing mercury is fitted in a position above the levels of taps B, C, and D which are in position IV, and the screw-clip G is opened so that the gas issues from the buret into the combustion tube at the rate of about 0.2 ml/min. During this operation the oxygen is passed through the side inlet. When the requisite amount of gas has been passed into the apparatus, the taps are turned to position V for 10 min, and the gas supply line swept with oxygen. The oxygen is passed for a further 10 min into the side inlet of the combustion tube, after which combustion is complete. The total time taken for a combustion is 25-30 min, for an oxygen throughput of about 20-25 ml/min.

## SUMMARY

A method is described for the simultaneous determination of fluorine, carbon, and hydrogen in volatile and gaseous compounds. It has been established that it is possible to take 4-9 mg samples of volatile liquids boiling at 20° and higher by means of quartz capillaries with open ends. A device is described which enables the capillaries containing samples to be opened outside the combustion tube, and a technique has been developed for taking samples of materials boiling in the range +20° to −45° in sealed capillaries.

## LITERATURE CITED

[1] M. O. Korshun, N. É. Gel'man, and K. I. Glazova, Doklady Akad. Nauk SSSR 111, 1225 (1956).*

[2] N. É. Gel'man, M. O. Korshun, and K. I. Novozhilova, Zhur. Anal. Khim. 15, 222 (1960).*

[3] N. É. Gel'man, M. O. Korshun, and K. I. Novozhilova, Zhur. Anal. Khim. 15, 342 (1960).*

[4] F. Pregl, Quantitative Organic Microanalysis [Russian translation] (Moscow, 1934) p. 66.

[5] L. J. Clark, Amer. Chem. Soc. 34, 746 (1912).

[6] S. Avery and D. Hayman, Ind. Eng. Chem. Analyt. Ed. 2, 336 (1930).

[7] H. Levin and K. Uhrig, Ind. Eng. Chem. Analyt. Ed. 9, 326 (1937).

[8] V. A. Aluise, Ind. Eng. Chem. Analyt. Ed. 10, 56 (1938).

[9] M. O. Korshun and N. É. Gel'man, New Methods of Elemental Microanalysis [in Russian] (Goskhimizdat, Moscow-Leningrad, 1949) p. 45.

[10] F. O. Fischer, Analyt. Chem. 21, 827 (1949).

[11] W. Schenk, Analyt. Chem. 26, 788 (1954).

[12] J. M. Corliss, Analyt. Chem. 29, 1902 (1957).

[13] R. N. McCoy and E. L. Bastin, Anal. Chem. 28, 1776 (1956).

[14] E. E. Reid, J. Amer. Chem. Soc. 34, 1037 (1912).

[15] J. R. Baily, Ind. Eng. Chem. Analyt. Ed. 5, 171 (1933).

[16] J. H. Bruun and W. B. M. Faulconer, Ind. Eng. Chem. Analyt. Ed. 8, 315 (1936)

[17] W. C. Schumb and K. J. Radimer, Anal. Chem. 20, 871 (1948).

[18] J. Pirsch, Ber. 65, 865 (1932).

* Original Russian pagination. See C. B. Translation.

# DETERMINATION OF PHENYL RADICALS IN SILICOORGANIC COMPOUNDS

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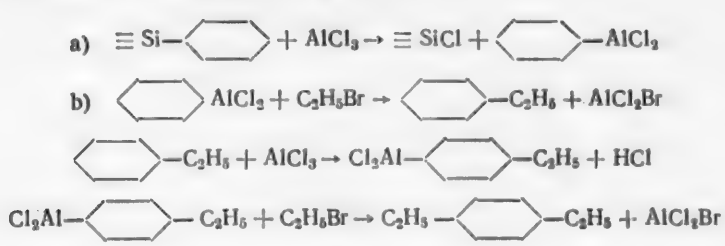
Methods for the analysis of silicoorganic compounds (SOC) have been described in detail [1, 2]. Physicochemical methods of determining radicals in SOC on the basis of their mass spectra [3, 4], and on the basis of their infrared and ultraviolet absorption spectra [5-9] have also been published. In view of the complexity of the methods indicated, however, they cannot always be used in laboratory practice. Until recently no chemical methods were known for the determination of radicals in SOC which would permit rapid and accurate control of the quality of the products obtained during the synthesis of high-molecular-weight SOC.

We have developed a new method for the quantitative determination of phenyl radicals in certain SOC; it is based on ethylation of phenyl-containing SOC by means of ethyl bromide in the presence of anhydrous aluminum chloride.

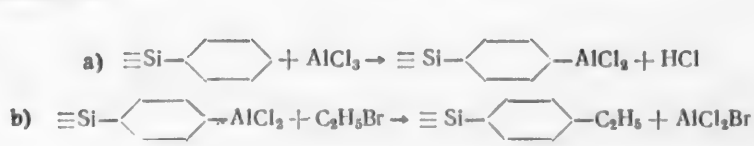
As our research showed, ethylation of SOC apparently proceeds according to two schemes:

Under the influence of $AlCl_3$ the Si–C bond is broken (a); this is accompanied by subsequent stepwise ethylation of the aluminoorganic compounds thereby obtained (b):



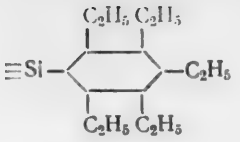
etc. Ethylation continues until hexaethylbenzene $C_6(C_2H_5)_6$ is formed.

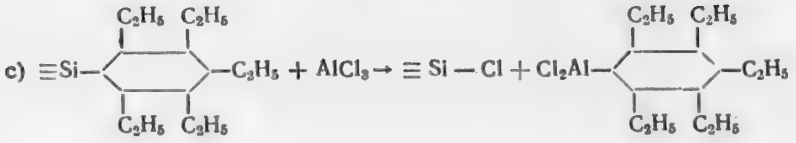
Under the influence of $AlCl_3$ formation of aluminosilicoorganic compounds (a) ethylated with ethyl bromide occurs (b). The process is completed by the breaking of the Si–C bond (c); this is accompanied by formation of hexaethylbenzene (d):

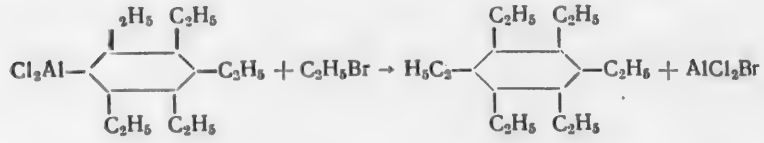


* A. A. Khvoshchevskaya and L. M. Kharchevnikova took part in the experimental work.

and so on right up to the formation of







On subsequent treatment of the reaction products with water, hexaethylbenzene containing other ethylated derivatives of benzene as impurities is obtained [10]. From the amount of the hexaethylbenzene formed it is possible to assess the content of phenyl groups in the original SOC. Hexaethylbenzene is characterized by a comparatively high average molecular weight and by its nonvolatility, which increase the experimental accuracy of the method. By observing constant ethylation conditions (concentration, temperature, and ethylation time) it is possible to obtain good reproducible results.

Our experiments on the ethylation of organic phenyl-containing compounds (benzene, diphenyl, toluene, etc.) with ethyl bromide in the presence of aluminum chloride have shown that it is also possible to use the ethylation reaction for the determination of benzene and its derivatives in organic compounds. Accordingly, the method suggested for the determination of phenyl groups may, probably, find use not only for SOC, but for other heteroorganic and organic compounds as well.

Our test materials were phenyltrichlorosilane, methylphenyldichlorosilane, polyphenylsiloxanes, polymethylphenylsiloxanes, and other SOC containing phenyl radicals directly connected to silicon atoms. Calculations of the original products were carried out on the basis of the following considerations. When the test SOC contains not more than one phenyl radical per structural unit of the original SOC, then 6-7 g (about 0.05 mole) of anhydrous aluminum chloride and 35-40 g of ethyl bromide (about 0.35 mole) are used for 2-2.5 g (about 0.01 mole) of the test SOC. When the test compound is likely to contain more than one phenyl radical per structural unit, the amounts of aluminum chloride and ethyl bromide are increased correspondingly. Ethyl bromide serves as solvent and ethylating reagent simultaneously. The test SOC and the calculated amounts of aluminum chloride and ethyl bromide are placed in a 200-250 ml round-bottom flask fitted with a ground-glass reflux condenser. The condenser is connected via a calcium chloride tube to a flask containing alkali solution which is used for absorbing HCl. The flask is placed in a thermostat the water in which is at a temperature of 30°. The reaction mixture is periodically shaken. Ethylation is carried on for two hours. At the end of this time the condenser is disconnected and 50 ml of distilled water added in small portions to the contents of the flask; the flask is cooled during this stage. When decomposition is complete the ethylated benzene derivatives are extracted with small portions (30-50 ml each) of diethyl ether, the amount of the latter taken being such that the total volume of the extract is 250 ml. The silicic acid precipitate is first separated by decantation and then by filtration. The extract obtained is washed with water until the water liquors give a neutral reaction, and the extract then distilled in a tared 50-100 ml Wurtz flask in order to distill off the solvents (diethyl ether and ethyl bromide). After distilling off the solvents, the flask plus its contents are placed in a vacuum desiccator containing $P_2O_5$. The isolated product is a solid material with a slightly yellowish color. The m. p. is 123-125°.

On recrystallizing the reaction product from ethanol and glacial acetic acid hexaethylbenzene is isolated and identified – white crystalline material (prisms), which is soluble in ether, benzene, toluene, in hot ethanol, and glacial acetic acid.

Found % C – 87.65; H – 12.35; mol. wt. 247; m. p. 126°
Calculated % C – 87.82; H – 12.35; mol. wt. 246; m. p. 126.5 (129°) [11].

The phenyl radical content is calculated by means of the formula:

$$C_6H_5 = \frac{a_e \cdot 77 \cdot 100}{a \cdot 246 \cdot K_e} = \frac{a_e \cdot 77 \cdot 100}{a \cdot 246 \cdot 0{,}91} = \frac{a_e \cdot 34{,}4}{a} \%,$$

where a is the weight of test material taken, in g; $a_e$ is the amount of the ethylated product, in g; 77 is the mol. wt. of the phenyl group; and 246 is the mol. wt. of hexaethylbenzene.

$K_e$ is the ethylation factor determined experimentally.

The ethylation factor is a correction to be applied for the purity of the ethylated product isolated and for the losses which occur during its isolation. The ethylation factor was determined by ethylating chemically pure phenyltrichlorosilane with a b. p. of 201°.

After carrying out the reaction, and the ethylated product has been brought to constant weight, the ethylation factor is calculated as: $K_e = M_e/M_h$ where $M_h$ is the mol. wt. of hexaethylbenzene and $M_e$ is the mol. wt. of the ethylated product:

$$M_e = \frac{M_{C_6H_5SiCl_3} a_e}{a},$$

where $M_{C_6H_5SiCl_3}$ is the mol. wt. of phenyltrichlorosilane.

In addition to phenyltrichlorosilane, the ethylation factor was also determined by means of methylphenyldichlorosilane, polyphenylsiloxane, and methylphenylpolysiloxane; the value thereby found for the ethylation factor was 0.91 ± 0.01.

Below are given elemental analyses which confirm the purity of the SOC used in our experiments.

| | | |
|---|---|---|
| $C_6H_5SiCl_3$ | Found %: | Si – 13.42; Cl – 50.40 |
| | Calculated %: | Si – 13.26; Cl – 50.29 |
| $C_7H_8SiCl_2$ | Found %: | Si – 14.51; Cl – 37.20 |
| | Calculated %: | Si – 14.69; Cl – 37.05 |
| $C_8H_{11}Si_2O_{2.5}$ | Found %: | C – 47.59; Si – 27.50; H – 6.05 |
| | Calculated %: | C – 47.30; Si – 27.64; H – 5.51 |
| $C_7H_8SiO$ | Found %: | C – 61.48; Si – 20.49; H – 6.034 |
| | Calculated %: | C – 61.73; Si – 20.71; H – 5.87 |

The phenyl-radical contents of test SOC are given in the following table.

| Formula of the test product | Sample wt., a, g | Found $a_e$, g | $C_6H_5$ content | | Error | M. p. of the ethylated product |
|---|---|---|---|---|---|---|
| | | | found | calc. | | |
| $C_6H_5SiCl_3$ | 2,10 | 2,18 | 36,14 | 36,44 | –0,30 | 123–125° |
| | 2,28 | 2,44 | 36,77 | 36,44 | +0,33 | |
| $CH_3C_6H_5SiCl_2$ | 2,12 | 2,58 | 41,04 | 40,15 | +0,89 | 123–124° |
| | 2,18 | 2,52 | 39,73 | 40,15 | –0,42 | |
| $[(CH_3)_2SiOC_6H_5SiO_{1,5}]_x$ | 2,19 | 2,35 | 36,91 | 37,69 | –0,78 | 122–124° |
| | 2,01 | 2,25 | 38,50 | 37,69 | +0,81 | |
| $[CH_3C_6H_5SiO]_x$ | 2,00 | 3,34 | 57,44 | 56,62 | +0,82 | 123–124° |
| | 2,14 | 3,43 | 55,14 | 56,62 | –1,42 | |

As is evident from the table, the results for the determination of phenyl radicals are reproducible to an accuracy of ± 1-1.5% (absolute).

## SUMMARY

A new method has been developed for the quantitative determination of phenyl radicals in silicoorganic compounds; it is based on the interaction of phenyl-containing silicoorganic compounds with ethyl bromide in the presence of anhydrous aluminum chloride.

It has been established that the interaction indicated is accompanied by ethylation of phenyl-containing silicoorganic compounds with ethyl bromide, by decomposition of the ethylated reaction products, and by formation of ethylated benzene derivatives.

## LITERATURE CITED

[1] A. P. Kreshkov, V. A. Bork, L. V. Myshlyaeva, and G. D. Nessonova, Analysis of Silicoorganic Compounds [in Russian] (Goskhimizdat, Moscow, 1954).

[2] A. P. Kreshkov and V. A. Bork, Uspekhi Khimii 28, 576 (1959).

[3] R. C. Taylor, A. Brown, W. S. Young, and C. E. Headington, Anal. Chem. 20, 396 (1948).

[4] C. A. Burkhard and F. J. Norton, Anal. Chem. 21, 304 (1949).

[5] A. P. Kreshkov, Yu. M. Mikhailenko, and G. F. Yakimovich, Zhur. Anal. Khim. 9, 208 (1954).*

[6] C. A. Burkhard and E. H. Winslow, J. Am. Chem. Soc. 72, 3276 (1950).

[7] A. P. Kreshkov, Yu. M. Mikhailenko, and I. P. Smirenkina, Zhur. Anal. Khim. 13, 834 (1958).*

[8] V. S. Fikhtengol'ts, Materials of a Technical Conference on the Chemistry and Practical Application of Silicoorganic Compounds, No. 3 [in Russian] (TsBTI, Leningrad, 1958) p. 27.

[9] H. Gilman and F. Marschall, J. Am. Chem. Soc. 71, 2066 (1949).

[10] A. P. Kreshkov, V. T. Shemyatenkova, S. V. Syavtsillo, and N. A. Palamarchuk, Author's Thesis No. 110684 15/V 1957.

[11] Beilstein 5, 358 (1943).

* Original Russian pagination. See C. B. Translation.

# SEPARATION OF THE LOWER ALIPHATIC ALDEHYDES AND KETONES BY PAPER CHROMATOGRAPHY, AND THEIR QUANTITATIVE DETERMINATION

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A method which has been developed for the identification and quantitative determination of the lower aliphatic alcohols ($C_1 - C_4$) by paper chromatography [1] has been successfully applied to the determination of the composition and amount of alcohols formed during the oxidation of n-butane at temperatures and pressures close to the critical values [2]. The problem which confronted us was to develop a technique for the qualitative and quantitative determination of carbonyl compounds in complex mixtures of the lower aliphatic aldehydes and ketones (formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, acetone, methyl ethyl ketone) which may be formed during the oxidation of n-butane. In order to solve this problem we used paper chromatographic separation of the corresponding 2,4-dinitrophenylhydrazones.

A large number of papers has been published on the chromatographic separation of carbonyl compounds by means of this method [3-10]. However, information on the separation of the mixtures of carbonyl compounds we are interested in is very sparse and is qualitative in nature [11, 12].

The possibility of carrying out quantitative determinations by means of paper chromatography has been examined earlier [13]. Experimental data on quantitative determination is only available for hydrazones of aromatic carbonyl compounds [14].

Separation of the 2,4-dinitrophenylhydrazones on ordinary chromatographic paper of the "Rapid Leningrad" type could not be achieved because of small differences in the properties of the hydrazones formed. In order to separate the mixture of aldehydes and ketones we are interested in, it is necessary to use paper which is hydrophobic in character; such paper is prepared by acetylation of the paper with acetic anhydride in a toluene solution [15-17].

The acetylating solution (1700 ml of toluene, 300 ml of acetic anhydride, and three drops of concentrated $H_2SO_4$) is poured into a 2 liter measuring cylinder, and sheets of chromatographic paper 120 × 300 $mm^2$ wound on a teflon spiral immersed in it. The measuring cylinder is placed in a thermostat, and at a temperature of 65-70° the reaction is complete in 8-10 hours. The paper is considered to be acetylated when a piece of it dissolves in chloroform. The paper is then washed in methanol until the odor of acetic acid is no longer detectable, and it is dried in air. The paper is soaked for 4-5 min in methanol prior to placing the test material on it; the methanol is used as the stationary phase; the mobile phase is hexane, heptane, or nonane. Hexane, heptane, or nonane is poured onto the bottom of the tank which is to be used for ascending chromatography (the efficiency of descending chromatography is equal to that of ascending chromatography) and a beaker containing methanol also placed on the bottom; the tank is hermetically sealed. In the course of 24 hours at a temperature of 20° the methanol saturates the mobile phase and the vessel is ready for use.

TABLE 1

$R_f$ Values for the 2,4-Dinitrophenylhydrazones of Formaldehyde, Acetaldehyde, Propionaldehyde, Butyraldehyde, Acetone, Methyl Ethyl Ketone for Various Solvents on Various Batches of Acetylated Paper

| Expt. No. | Paper batch | Mobile phase | $R_f$ (20°, $l$=300 mm) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | formaldehyde | acetaldehyde | propionaldehyde | butyraldehyde | acetone | methyl ethyl ketone | 2,4-dinitrophenylhydrazine |
| 1 | I | Hexane | 0,26 | 0,38 | 0,62 | 0,90 | 0,52 | 0,75 | 0,00 |
| 2 | I | Heptane | 0,06 | 0,15 | 0,35 | 0,69 | 0,29 | 0,50 | 0,00 |
| 3 | I | Heptane | 0,07 | 0,20 | 0,36 | 0,60 | 0,23 | 0,48 | 0,00 |
| 4 | I | Heptane | 0,03 | 0,18 | 0,32 | 0,58 | 0,26 | 0,48 | 0,00 |
| 5 | I | Nonane | 0,06 | 0,16 | 0,30 | 0,54 | 0,25 | 0,39 | 0,00 |
| 6 | II | Heptane | 0,07 | 0,17 | 0,42 | 0,82 | 0,35 | 0,61 | 0,00 |
| 7 | III | Heptane | 0,04 | 0,10 | 0,24 | 0,46 | 0,19 | 0,33 | 0,00 |
| 8 | III | Hexane | 0,18 | 0,30 | 0,54 | 0,92 | 0,45 | 0,80 | 0,00 |
| 9 | Published data [12] | Heptane | 0,09 | 0,18 | 0,32 | 0,42 | 0,30 | 0,43 | |

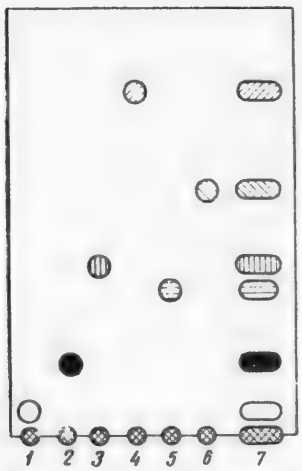


Fig. 1. Chromatogram of the 2,4-dinitrophenylhydrazones of the lower aliphatic aldehydes and ketones. 1) Formaldehyde; 2) acetaldehyde; 3) propionaldehyde; 4) butyraldehyde; 5) acetone; 6) methyl ethyl ketone; 7) a mixture of formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, acetone, and methyl ethyl ketone. The excess of 2,4-dinitrophenylhydrazine remains on the starting line.

The method was developed with the aid of synthetic mixtures of formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, acetone, and methyl ethyl ketone. The hydrazones were prepared by interaction of the corresponding carbonyl compound with 2,4-dinitrophenylhydrazine in a methanol solution in a weakly acid medium, with subsequent heating at a temperature of 60° for one hour. Excess 2,4-dinitrophenylhydrazine, as shown below, does not interfere with the separation of the hydrazones. The solution containing the 2,4-dinitrophenylhydrazones is placed on a sheet of the acetylated paper in a thin strip or as a spot at a distance of 20 mm from the edge of the paper; the paper is then placed in the chromatographic tank. Good separation of the bands is achieved by placing amounts of the order of $10^{-6}$ g·mole of the 2,4-dinitrophenylhydrazones on the paper; larger amounts lead to overloading of the paper, and, accordingly, no separation is achieved.

Complete separation of the compounds on a chromatogram at 20° is achieved in 3-4 hours; when the temperature is increased the rate of separation increases, but the definition of separation deteriorates. A typical chromatogram for a mixture of the 2,4-dinitrophenylhydrazones of formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, acetone, and methyl ethyl ketone is shown in Fig. 1. The presence of other oxidation products (peroxides, alcohols, acids, esters) and water in amounts which are normally formed during the oxidation of hydrocarbons, does not interfere with the separation of the hydrazones. The $R_f$ values obtained at 20° are given in Table 1. However, for strict identification of the test hydrazones, it is necessary to place on the same paper as that used for separating the hydrazones reference standards of the pure hydrazones of the corresponding carbonyl compounds, since on switching from one batch of acetylated paper to another, the $R_f$ values vary strongly with the quality of the paper obtained by acetylation. The reproducibility of experiments carried out on the same batch of acetylated paper is quite satisfactory (see the $R_f$ values for experiments 2 and 4 in Table 1).

When nonane, heptane, and hexane are used as the mobile phase, the $R_f$ values (and, consequently, the differences between adjacent $R_f$ values) increase with decreasing molecular weight of the hydrocarbon (Table 1). However, the efficiency of separation remains almost the same in all

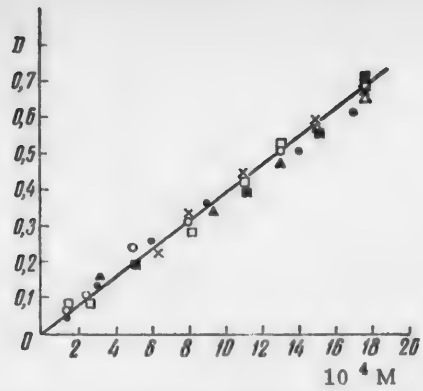


Fig. 2. Calibration curve for the quinoid forms of the 2,4-dinitrophenylhydrazones. ○) Formaldehyde; ●) acetaldehyde; □) propionaldehyde; ■) butyraldehyde; ×) acetone; ▲) methyl ethyl ketone.

TABLE 2

Separation and Quantitative Determination of Carbonyl Compounds from Their Synthetic Mixtures in Methanol

| Compound | Taken in the mixture ($M \cdot 10^6$) | Found ($M \cdot 10^6$) | |
|---|---|---|---|
| | | expt. no. 1 | expt. no. 2 |
| Formaldehyde | 12.2 | 12.4 | 12.6 |
| Acetaldehyde | 10.6 | 10.8 | 11.0 |
| Propionaldehyde | 8.6 | 8.2 | 8.7 |
| Butyraldehyde | 6.4 | 6.0 | 6.8 |
| Acetone | 8.6 | 8.4 | 9.0 |
| Methyl ethyl ketone | 6.4 | 7.0 | 6.9 |

cases, since, at the same time, the diffuseness of the spots of the test hydrazones increases. The $R_f$ value for 2,4-dinitrophenylhydrazine is always 0.00. After developing the chromatograms with a 5% solution of alcoholic alkali, all the hydrazones are colored a yellow-brown.

Quantitative determination of the 2,4-dinitrophenylhydrazones of the carbonyl compounds isolated from the mixtures was carried out on the basis of the light absorbed by the colored compounds with a quinoid structure which are formed on developing the chromatogram of the corresponding hydrazones. After development, the spot was cut out and the quinoid compounds of the 2,4-dinitrophenylhydrazones extracted with 5 ml of a 5% solution of KOH in methanol. The optical density of the solutions was measured on a SF-4 spectrophotometer or on a FÉK N-54 photocolorimeter at 480 mμ.

The amount of the carbonyl compounds is found from a calibration curve. We constructed such a calibration curve for formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, acetone, and methyl ethyl ketone at concentrations ranging from $1.5 \cdot 10^{-4}$ to $17.6 \cdot 10^{-4}$ M (Fig. 2). The calibration curves for all the compounds are almost the same and are straight lines, this is in agreement with published results [18].

Results of the separation and quantitative analysis of synthetic mixtures of the carbonyl compounds are given in Table 2.

The method suggested gives completely satisfactory results. The experimental error for the determination of aldehydes and ketones does not exceed 6%. Only in the case of methyl ethyl ketone does this error amount to 10%.

The author wishes to thank N. M. Émanuél' and Z. K. Maizus for valuable advice in carrying out this work.

## SUMMARY

A method has been developed for the paper chromatographic separation and quantitative determination of the 2,4-dinitrophenylhydrazones of formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, acetone, and methyl ethyl ketone. The presence of water and other products resulting from the oxidation of hydrocarbons does not interfere in the quantitative determination of the carbonyl compounds.

## LITERATURE CITED

[1] G. E. Zaikov, Zhur. Anal. Khim. 15, 104 (1960).*

[2] N. M. Émanuél', Doklady Akad. Nauk SSSR 110, 245 (1956).*

[3] R. G. Rice, G. J. Keller, and J. G. Kirchner, Analyt. Chem. 23, 194 (1951).

* Original Russian pagination. See C. B. Translation.

[4] H. S. Burton, Chem. and Ind. 20, 571 (1954).

[5] V. Sykora and Z. Prochazka, Chem. Listy 47, N 11, 1674 (1953).

[6] S. M. Altmann, E. M. Cook, and S. P. Datta, Biochem. J. 49, 93 (1951).

[7] D. Cavallini, N. Frontali, and G. Toschi, Nature 163, 568 (1949).

[8] D. Cavallini, N. Frontali, and G. Toschi, Nature 164, 792 (1949).

[9] I. V. Kostir and K. Slavik, Collection Czechoslov. Chem. Commun. 15, 17 (1950).

[10] W. J. Schmitt, S. J. Mariconi, and W. F. O'Connor, Analyt. Chem. 28, 249 (1956).

[11] W. S. Lynn, L. A. Steele, and E. Staple, Analyt. Chem. 28, 132 (1956).

[12] D. F. Meigh, Nature 170, 579 (1952).

[13] J. Bouzkova, M. Heitmanek, and I. Vovruch, Chem. Listy 51, 36 (1957).

[14] V. L. Pikaeva, Zhur. Anal. Khim. 14, 184 (1959).*

[15] R. I. Boscott, Nature 159, 342 (1947).

[16] M. S. Burton, Chem. and Ind. 46, 1229 (1953).

[17] M. B. Neiman, V. M. Levkovskii, and A. F. Lukovnikov, Doklady Akad. Nauk SSSR 81, 841 (1951).

[18] G. R. Lappin and L. C. Clark, Analyt. Chem. 23, 541 (1951).

* Original Russian pagination. See C. B. Translation.

# BRIEF COMMUNICATIONS

## THE MASS-SPECTROMETRIC ANALYSIS OF THE ISOTOPIC COMPOSITION OF ELEMENTAL BORON

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Determination of the isotopic composition of elemental boron is of practical importance. We have developed a technique for the isotopic analysis of boron by evaporating it from the ribbon evaporator of the ion source of a mass spectrometer, and subsequent ionization of the vapors obtained by electronic impact. A type MI-1301 mass spectrometer provided with an evaporating block was used in the course of the work. Measurement were carried out by a single-beam method. The ion source did not differ in constructional details from that described previously [1]. Bearing in mind the high boiling point of boron, tungsten foil 0.02 mm thick was used for making the evaporator; the shape of the evaporator was the same as that of a platinum evaporator [2].

About 0.1 mg of boron in the form of an alcoholic suspension was placed on the evaporator. This amount is sufficient for continuous work for 5-6 hours with completely satisfactory stability of the ion currents. Since the relationship between the temperature of the evaporator and the heating current of the block had not been determined beforehand, the requisite boron vapor pressure in the anode compartment of the ion source was achieved by regular [1] elevation of the evaporator temperature until an ion current of the highest intensity for the expected effective masses – about 1000-1500 mv – was obtained.

In the mass spectrum of the vapors above the boron, $B^+$ ions were discovered; these were used for calculating the isotopic composition of the test sample. Results for the analysis of elemental boron with a natural content of its isotopes are given in Table 1.

The boron was prepared from boric acid by reduction with magnesium [3]. The chemical purity of the product obtained in this way was not less than 86% with respect to the content of the main material. The boric acid used as an initial product for the preparation of elemental boron was also subjected to isotopic analysis by a method described in [2]. The results of these experiments are also given in Table 1.

Several samples of elemental boron enriched with the $B^{10}$ isotope were analyzed by the method developed. These results are given in Table 2. As in the case of the analysis of boron with a natural content of its isotopes, these experiments were controlled by an analysis of the original product.

As is evident from Tables 1 and 2, the experimental results for the isotopic composition of elemental boron, obtained at different times are reproducible with a reasonable accuracy and agree very well with the results obtained during the analysis of boric acid.

In the course of an analysis, part of the boron is scattered on the details of the ion source of the mass spectrometer, and this affects the experimental accuracy of the isotopic composition of boron during the analysis of subsequent samples. In order to eliminate this effect it is sufficient to boil the anode compartment and the evaporator holder in a 3% solution of hydrogen peroxide, and then wash them with alcohol.

During the analyses attention was given to the evaporation process of boron from the ribbon evaporator. In the diagram a curve is shown which characterizes the change in the value of the ratio $B^{11}/B^{10}$ during the

TABLE 1

Isotopic Composition of Boron in a Sample with a Natural Content of Its Isotopes

| Date of measurement | $B^{11}/B^{10}$ in the boron sample* | $B^{11}/B^{10}$ in a sample of boric acid |
|---|---|---|
| 5. I—1959 | 4,17±0,02 | 4,18±0,04 |
| 30. I—1959 | 4,18±0,01 | 4,16±0,03 |
| 04.II—1959 | 4,17±0,01 | 4,18±0,03 |
| 10.II—1959 | 4,17±0,01 | 4,18±0,02 |
| 16.II—1959 | 4,18±0,01 | 4,16±0,03 |

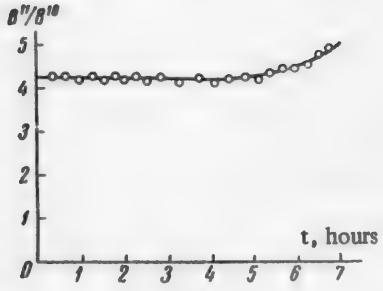
*Mean of 20-25 measurements.

TABLE 2

Isotopic Composition of Boron in Samples Enriched with $B^{10}$

| Sample No. | $B^{11}/B^{10}$ in boron* | $B^{11}/B^{10}$ in boric acid |
|---|---|---|
| 1 | 0,222 ± 0,001 | 0,222 ± 0,004 |
| 2 | 0,224 ± 0,004 | 0,226 ± 0,008 |
| 3 | 0,219 ± 0,002 | 0,222 ± 0,006 |
| 4 | 0,197 ± 0,002 | 0,200 ± 0,004 |
| 5 | 0,184 ± 0,003 | — |
| 6 | 0,207 ± 0,001 | 0,205 ± 0,005 |
| 7 | 0,168 ± 0,002 | 0,165 ± 0,003 |

*Mean of 20-25 measurements.




The relation between the value of the ratio $B^{11}/B^{10}$ and time.

analysis. Four to five hours after the start of the evaporation process, the value of the ratio $B^{11}/B^{10}$ starts to increase appreciably; this indicates that normal fractionation of the boron isotopes occurs during evaporation. This ratio is constant at the beginning of an experiment. Thus, the value of the isotopic fractionating effect during evaporation of boron is lower than the error of our measurements in the course of 4-5 hours from the beginning of an analysis, and does not affect the accuracy of the determination of the isotope ratio in boron. Results obtained at the end of an analysis cannot give the true ratio of the boron isotopes in the test sample.


SUMMARY

The method of evaporating from a ribbon-evaporator has been used during the mass-spectrometric isotopic analysis of elemental boron.

The isotopic composition of boron with natural and modified ratios of the isotopes has been measured. The results have been checked by comparing them with measurements of the isotopic composition of the boron in the starting material ($H_3BO_3$).

Evaporation of boron from the ribbon evaporator has been studied. It was found that during the evaporation of boron, normal fractionation of the isotopes of the latter is observed. The influence of the fractionating effects indicated on the accuracy of the determination of the isotopic composition of boron has been studied.

## LITERATURE CITED

[1] L. E. Levina, Pribory i Tekhn. Éksp. No. 5, 114 (1957).

[2] G. A. Semenov and Yu. A. Zonov, Zhur. Anal. Khim. 14, 137 (1959).*

[3] A. S. Mikulinskii, V. V. Efresikin, S. S. Sheveleva, and A. P. Sachko, Trudy Ural'skovo Nauch.-Issled. Khim. Inst. 5, 166 (1957).

* Original Russian pagination. See C. B. Translation.

# TITRIMETRIC DETERMINATION OF NITRATES IN WATER

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The method described below for the determination of nitrates is based on their conversion into nitro derivatives of phenoldisulfonic acid, with subsequent titration of the latter with a solution of methylene blue in the presence of benzene, which quantitatively extracts the interaction products of the nitrophenyl derivatives and methylene blue. The low solubility of methylene blue picrate in water and its very good solubility in chloroform was noted by Rose in 1917 and was used by Bolliger [1] for developing a titrimetric method for the determination of picric acid. Bolliger [2] established that it is possible to determine the following dinitrophenols in the same way: 2,4-dinitrophenol, 2,6-dinitrophenol, 2,6-dinitroparacresol, 2,4-dinitroresorcinol, and 2,4-dinitro-α-naphthol; he noted, however that this method is not applicable to other nitrophenols.

During titration of methylene blue a compound of nitrophenol methylene blue is formed with a molar ratio of 1:1 of the components; on shaking, this compound immediately passes into the chloroform. When all the nitrophenol has reacted, the aqueous layer acquires a blue color. During this process the color changes as follows: yellow, yellow-pale greenish, yellow-green, green, and blue. A more clearly defined color change is observed with picric acid than with nitrophenols.

During determination of nitrates, after their conversion into the nitro derivatives, on titration with methylene blue using chloroform, the aqueous phase is colored green right from the beginning of titration; this color gradually increases, but the change from green to blue is difficult to establish. In order to increase the clarity of the color change, we tried various solvents and settled on benzene.

Extraction is incomplete in a neutral medium; the benzene layer remains almost colorless. In an alkaline medium the benzene layer is colored violet right from the beginning. The optimum medium for carrying out the reaction is a weakly alkaline medium which is 0.003-0.006 N with respect to NaOH added in excess after neutralization until the maximum yellow color is obtained. Under these conditions the reproducibility is completely satisfactory. NaOH concentrations which are 1-2 times greater or less than that indicated do not affect the results. When the NaOH concentration is five times greater, the results obtained are 5% too high, while for a concentration which is five times less the results obtained are 5% too low (Table 1).

The methylene blue solution is standardized against a solution containing a known concentration of $NO_3^-$. The color of the aqueous layer during titration with methylene blue in the presence of benzene changes as follows: greenish-yellow, green – the green is less intense than when chloroform is used – and then green-blue, and, finally blue. The change from green through green-blue to blue complicates determination of the end point of the titration.

From numerous experiments with concentrations differing by approximately five times from each other (Table 2), it follows that the bluish-green color of the aqueous layer which is observed up to 10-15% from the end point differs clearly from the blue color at the end point.

In order to establish the end point, separate titration of two similar samples should be carried out, in which the volume of reagent added to each sample differs by 0.1-0.2 ml. By using this technique it is possible to

TABLE 1

| Solvent | $NO_3^-$ taken, mg | NaOH concentration, N | Amount of 0.001 M methylene blue used, ml | | |
|---|---|---|---|---|---|
| | | | to the green color | to the green-blue color | to the end point |
| $CHCl_3$ | 0,31 | — | 2,5 | 2,7 | ~3 |
| $CHCl_3$ | 0,31 | 0,5—0,6 | 2,8 | 3,3 | ~4 |
| $CHCl_3$ | 0,31 | 1,5—0,6 | 2,8 | 3,3 | ~4,2 |
| $C_6H_6$ | 0,31 | — | 2,2 | 2,4 | ~3 |
| $C_6H_6$ | 0,31 | 0,25—0,6 | 3,2 | 3,5 | 3,8±0,1—0,2 |
| $C_6H_6$ | 0,31 | 0,5—0,6 | 3,3 | 3,5 | 3,8±0,1—0,2 |
| $C_6H_6$ | 0,31 | 1,5—0,6 | 3,3 | 3,5 | 3,8±0,1—0,2 |
| $C_6H_6$ | 0,155 | 0,1—0,6 | 1,3 | 1,6 | 1,8±0,1 |
| $C_6H_6$ | 0,155 | 0,5—0,6 | 1,4 | 1,6 | 1,9±0,1 |
| $C_6H_6$ | 0,155 | 2,5—0,6 | 1,4 | 1,7 | 2±0,1 |

TABLE 2

(1 ml of the methylene blue corresponds to 0.081 ± 0.004 mg $NO_3^-$)

| $NO_3^-$ taken, mg | 0,6 N NaOH added, ml | 0.001 M methylene blue solution used | | |
|---|---|---|---|---|
| | | to the green color | to the green-blue color | to the end point |
| 0,31 | 0,5 | 3,3 | 3,5 | 3,8±0,1—0,2 |
| 0,31 | 0,5 | 3,3 | 3,5 | 3,8±0,1—0,2 |
| 0,155 | 0,5 | 1,4—1,5 | 1,6 | 1,9±0,05—0,1 |
| 0,155 | 0,5 | 1,4—1,5 | 1,6 | 1,9±0,05—0,1 |
| 0,0775 | 0,5 | 0,6—0,7 | 0,8 | 0,95±0,03—0,05 |
| 0,0775 | 0,5 | 0,3 | 0,4 | 0,475±0,025 |

TABLE 3

| $NO_3^-$ added, mg | $NO_3^-$ found, mg |
|---|---|
| 0,31 | 0,30 |
| 0,31 | 0,32 |
| 0,62 | 0,59 |
| 0,62 | 0,62 |

titrate with an accuracy of ± 5%. After some practice, when it is possible to decrease the difference between the volumes of reagent added to each sample, the experimental accuracy increases.

In order to check this method, determinations were carried out on samples of natural water free from nitrates but to which was added known amounts of $NO_3^-$ (Table 3). The composition of the water* was as follows: $NH_3$ absent, $NO_2^-$ absent. Oxidizability 9 mg of $KMnO_4$/liter; $HCO_3$ = 490 mg/liter; $Cl^-$, 12 mg/liter; $SO_4^{2-}$, 18 mg/liter; $Ca^{2+}$, 90 mg/liter; $Mg^{2+}$, 24 mg/liter.

Analytical procedure. Reagents. The phenoldisulfonic acid is prepared by heating 25 g of phenol crystals with 150 ml of $H_2SO_4$ sp.gr. 1.84 for six hours on a water bath under reflux. 0.001 M methylene blue solution. 0.01 M $KNO_3$ solution. $Ag_2SO_4$ solution (4.937 g/liter), 1 ml corresponds to 1 mg $Cl^-$.

The test water containing 0.1-1 mg $NO_3^-$, after precipitation of chlorides by addition of $Ag_2SO_4$,** is evaporated in a porcelain basin on a water bath. To the cooled precipitate is added 1 ml of phenoldisulfonic acid and the mixture stirred with a glass rod. It is allowed to stand for 10 min. 5-10 ml of distilled water is added. The solution is neutralized with 6 N NaOH by addition of the latter dropwise almost to the equivalence point. Addition of 0.6 N NaOH is continued until the liquid has a yellow color which does not increase in intensity on addition of a further drop of 0.6 N NaOH. The mixture is transferred to a 50 or 100 ml standard flask, the basin being washed out 3-4 times with distilled water. Into two similar cylindrical separating funnels or

* The chlorine was removed with silver sulfate.

** For details of preparing the samples, see [3-4].

into two conical flasks fitted with glass stoppers are introduced equal volumes of the nitrophenolate solution. 0.5 ml of 0.6 N NaOH is added to each of them and the volume made up to 50-100 ml with distilled water. Benzene is added (the benzene and aqueous layers should have the same volume in both vessels).

Both samples are titrated in parallel with 0.001 N methylene blue solution added in 0.1-0.2 ml lots and shaken vigorously after each addition. The aqueous layer initially has a yellow-greenish color and then becomes green, while the benzene layer has a violet color. Starting from the point at which the aqueous layer acquires an intense green color or a green with a blue tinge, titration is continued by addition of 0.1-0.2 ml more of the reagent to one sample than to the other. The end point is taken as that point at which the aqueous layer has a pure blue tinge. In the case of the sample to which less reagent has been added, the aqueous layer should have a bluish-greenish color, while in the case of the sample to which more reagent has been added the color of the aqueous layer should be blue.

The methylene blue solution is standardized against a standard $KNO_3$ solution.

Titration should be carried out at approximately the same rate.

## SUMMARY

A method suggested for the determination of nitrates is based on their conversion to nitro derivatives of phenoldisulfonic acid, this is followed by titration with methylene blue solution in the presence of benzene which quantitatively extracts the interaction products of the nitrophenol derivative and methylene blue.

## LITERATURE CITED

[1] A. Bolliger, J. Proc. Roy. Soc. of New South Wales 67, 240 (1930); Z. analyt. Chem. 105, 48 (1936); C II, 3961 (1935).

[2] A. Bolliger, J. Proc. Roy. Soc. of New South Wales 68, 51 (1935); Z. analyt. Chem. 111, 124 (1936); C II, 2451 (1939).

[3] Skopintsev, Z. analyt. Chem. 85, 244 (1931).

[4] GOST 4192/1948.

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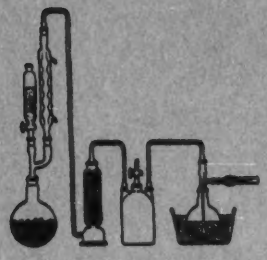

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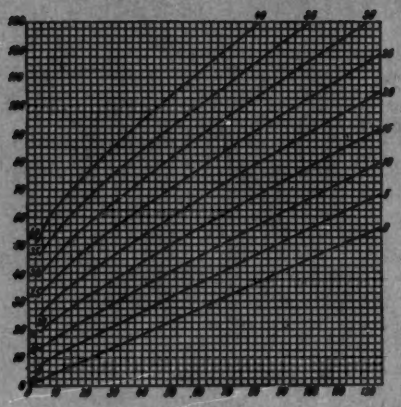

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by I. Yu. Sokolov

Translated from Russian

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All the tables and nomograms are based on analytical results expressed in the form widely used in hydrogeological practice—milligrams per liter (weight form) and milligram-equivalents per liter (equivalent form). For calculation of percent-equivalents, the sum of cation equivalents and the sum of anion equivalents are taken as 100% each. Several new tables are presented for the first time, and the many tables for converting water-analysis results from one form to another make it possible to find the milligram-equivalents for any practically possible content of a component in water, accurate to the second decimal place, and the weight content of substances to tenths of a milligram.

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III. Tables for converting milligrams into milligram-equivalents

IV. Tables for converting milligram-equivalents into milligrams

V. Tables for converting oxides to ions

VI. Tables for converting nitrogen into nitrogen-containing ions

VII. Table for converting milligrams of $NH_3$ into milligrams of $NH_4^+$

VIII. Table for converting oxidizability with milligrams of $KMnO_4$ into milligrams of O

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